


State Equations

	Reading	Problems
	3-6, 3-7, 4-3 → 4-5	3-59, 3-68, 3-80
	6-6	
	7-3, 7-4, 7-7 → 7-10	7-38, 7-98, 7-143, 7-163

The Thermodynamics of State

IDEAL GAS

The defining equation for an ideal gas is

$$\frac{Pv}{T} = \text{constant} = R$$

Knowing that $v = V/m$

$$\frac{PV}{Tm} = \text{constant} = R$$

where R is a gas constant for a particular gas (as given in C&B Tables A-1 and A-2).

An Isentropic Process for an Ideal Gas

Given:

- constant specific heats over a wide range of temperature
- $ds = 0$
- $du = c_v dT \equiv c_v = \left(\frac{\partial u}{\partial T} \right)_v$
- $dh = c_p dT \equiv c_p = \left(\frac{\partial h}{\partial T} \right)_p$

Gibb's equation can be written as

$$Tds = du + Pdv = c_v dT + Pdv = 0 \quad (1)$$

where $ds = 0$ because we have assumed an isentropic process.

The definition of enthalpy is

$$h = u + Pv$$

Taking the derivative yields

$$dh = \underbrace{du + Pdv}_{\equiv Tds} + vdP$$

$$dh = Tds + vdP \Rightarrow Tds = 0 = dh - vdP$$

$$\boxed{c_p dT - vdP = 0} \quad (2)$$

Equating Eqs. (1) and (2) through the dT term gives

$$\frac{dP}{P} = -\frac{c_p}{c_v} \frac{dv}{v} \quad (3)$$

Integrating (3) from its initial state to a final state

$$P_1 v_1^k = P_2 v_2^k = \text{constant} = Pv^k$$

where

$$k = \frac{c_p}{c_v}$$

The product of $P \cdot v^k$ remains constant for an ideal gas when:

- specific heats are constant

- the gas undergoes an isentropic process \rightarrow reversible + adiabatic

Combining this result with the ideal gas equation of state

$$\boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}}$$

The isentropic process is a special case of a more general process known as a polytropic process

where $\rightarrow Pv^n = \text{constant}$ and n is any number.

Special Cases

- $n = 1$ $Pv = RT = \text{constant} \Rightarrow$ isothermal process
- $n = 0$ $Pv^0 = \text{constant} = P \Rightarrow$ isobaric process (constant pressure)
- $n = k$ $Pv^k = \text{constant} \Rightarrow$ isentropic process ($k = c_p/c_v$)
- $n = \infty$ $Pv^\infty = \text{constant} \Rightarrow$ isochoric process (constant volume)

Relative Pressure and Relative Specific Volume

- typically we assume specific heat to be constant with respect to temperature
- *but* when temperature swings are significant, this assumption can lead to inaccuracies, i.e.

T (K)	c_p (kJ/kg · K)	% difference
300	1.0057	
1000	1.1417	13.5
2500	1.688	67.8

- the relative pressure and relative volume tables (C&B Table A-17), provide an accurate way of including the temperature effects on specific heat for ideal gases during isentropic processes
- note: the specific heat ratio term given by $k = c_p/c_v$ will also be influenced by temperature

- **Procedure:**

- given T_1 , P_1 and P_2 for an isentropic process
- determine P_{r1} at T_1 from Table A-17
- calculate P_{r2} , where

$$\left(\frac{P_2}{P_1}\right)_{s=const} = \frac{P_{r2}}{P_{r1}}$$

- read T_2 from Table A-17 for the calculated value of P_{r2}

- use a similar procedure if volume is known instead of pressure, where

$$\left(\frac{v_2}{v_1}\right)_{s=const} = \frac{v_{r2}}{v_{r1}}$$

In Summary

For an ideal gas with constant c_p and c_v

$$Pv = RT$$

$$u_2 - u_1 = c_v(T_2 - T_1)$$

$$h_2 - h_1 = c_p(T_2 - T_1)$$

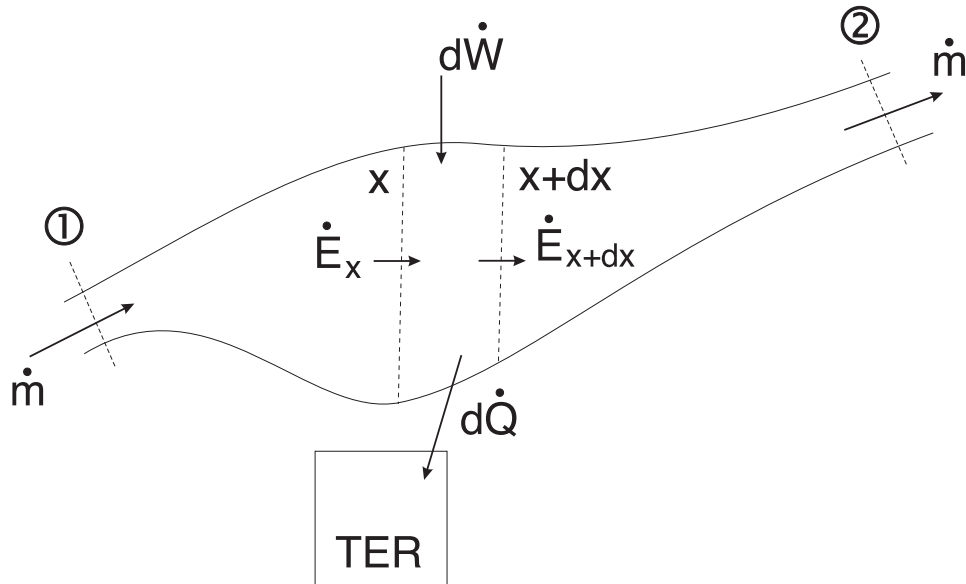
There are 3 forms of a change in entropy as a function of T & v , T & P , and P & v .

$$\begin{aligned} s_2 - s_1 &= c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \\ &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ &= c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{P_2}{P_1} \end{aligned}$$

$$R = c_p - c_v$$

A General Formulation

Steady State, Steady Flow in a Flow Channel of Arbitrary Cross-section with Work and Heat Transfer



$$\begin{aligned} d\dot{E} &= \dot{E}_{final} - \dot{E}_{initial} \\ &= \dot{E}_{x+dx} - \dot{E}_x \end{aligned}$$

where

$$\begin{aligned} \dot{E} &= \dot{m}(e + Pv) \\ &= \dot{m}\left(u + \frac{(v^*)^2}{2} + gz + Pv\right) \end{aligned}$$

From the 1st law

$$\text{rate of energy storage} = \text{rate of work} + \text{rate of heat transfer} + \text{net rate of energy leaving the system}$$

$$\frac{dE_{cv}}{dt} = d\dot{W} - d\dot{Q} - d\dot{E} \quad (1)$$

where $\frac{dE_{CV}}{dt} = 0$ for steady state.

Equation (1) becomes

$$0 = d\dot{W} - d\dot{Q} - \dot{m} d \left[u + Pv + \frac{(v^*)^2}{2} + gz \right] \quad (2)$$

From the 2nd law

$$\begin{array}{l} \text{rate of} \\ \text{entropy} \\ \text{storage} \end{array} = \left\{ \begin{array}{l} \text{rate of} \\ \text{entropy} \\ \text{inflow} \end{array} - \begin{array}{l} \text{rate of} \\ \text{entropy} \\ \text{outflow} \end{array} \right\} + \begin{array}{l} \text{rate of} \\ \text{entropy} \\ \text{production} \end{array}$$

$$\frac{dS_{CV}}{dt} = [\dot{m}s]_x - [\dot{m}s]_{x+dx} - \frac{d\dot{Q}}{T_{TER}} + \dot{\mathcal{P}}_S$$

where $\frac{dS_{CV}}{dt} = 0$ for steady state.

$$0 = -\dot{m}ds - \frac{d\dot{Q}}{T_{TER}} + \dot{\mathcal{P}}_S$$

or

$$d\dot{Q} = T_{TER}\dot{\mathcal{P}}_S - T_{TER}\dot{m}ds \quad (3)$$

Combining (2) and (3) through $d\dot{Q}$

$$\boxed{T_{TER}\dot{\mathcal{P}}_S - T_{TER}\dot{m}ds = d\dot{W} - \dot{m} d \left(u + Pv + \frac{(v^*)^2}{2} + gz \right)} \quad (4)$$

Equation (4) can be used for any SS-SF process.

Special Cases

Reversible, SS-SF Process

Reversible implies $\Rightarrow \dot{\mathcal{P}}_S = 0$

- frictionless process
- heat transfer is allowed but must be across $\Delta T \rightarrow 0$
- which means $T_{TER} \approx T_{CV} = T$

Equation 4 becomes

$$\frac{d\dot{W}}{\dot{m}} = -Tds + \underbrace{\frac{du + d(Pv)}{=du + Pdv + vdP}}_{=Tds} + d\left(\frac{(v^*)^2}{2}\right) + d(gz) \quad (5)$$

Therefore

$$\frac{d\dot{W}}{\dot{m}} = vdP + d\left(\frac{(v^*)^2}{2}\right) + d(gz) \quad (6)$$

Integrating Eq. (6) between the inlet and the outlet

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} vdP + \underbrace{\frac{(v^*)^2}{2}}_{\Delta KE} \Big|_{in}^{out} + \underbrace{gz}_{\Delta PE} \Big|_{in}^{out} \quad (7)$$

but ΔKE and ΔPE are usually negligible.

If $\Delta KE + \Delta PE = 0$

$$\boxed{\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} vdP} \quad (8)$$

Equation can be used for a reversible, SS-SF flow in a liquid or a gas.

If we keep in mind

$$\rho_{liq} \gg \rho_{gas} \Rightarrow v_{liq} \ll v_{gas}$$

i.e. water @ 25 °C $\rho = 997 \text{ kg/m}^3$ and air @ 25 °C $\rho = 1.18 \text{ kg/m}^3$

Therefore

$$\left(\frac{\dot{W}}{\dot{m}}\right)_{liq} \ll \left(\frac{\dot{W}}{\dot{m}}\right)_{gas}$$

For example: the work required to operate a pump is much less than that required to operate a compressor.

Incompressible Substance

This is a special case of Eq. (8) where $v = \text{constant} = v_{in} = v_{out}$.

From Equation (8)

$$\frac{\dot{W}}{\dot{m}} = v_{in}(P_{out} - P_{in}) \quad (9)$$

The work term represents the minimum work required to pump a liquid from P_{in} to P_{out} with negligible ΔKE and ΔPE .

Incompressible Substance and $d\dot{W} = 0$

From Eq. (6)

$$v dP + d\left(\frac{(v^*)^2}{2}\right) + d(gz) = 0 \quad (10)$$

Therefore

$$d\left(\frac{P}{\rho}\right) + d\left(\frac{(v^*)^2}{2}\right) + d(gz) = 0$$

$$d \left(\frac{P}{\rho} + \frac{(v^*)^2}{2} + gz \right) = 0 \quad (11)$$

Integrating gives

$$\frac{P}{\rho} + \frac{(v^*)^2}{2} + gz = \text{constant} \quad (12)$$

Equation (12) is Bernoulli's equation for frictionless flow with constant density. The constant is Bernoulli's constant, which remains constant along a streamline for steady, frictionless, incompressible flow.

Isothermal Ideal Gas, Compression/Expansion

This is a special case of Eq. (8) for an ideal gas where $Pv = RT$

$$Pv = \text{constant} = (Pv)_{in} = (Pv)_{out}$$

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v dP = \int_{in}^{out} (Pv)_{in} \frac{dP}{P}$$

Therefore

$$\boxed{\frac{\dot{W}}{\dot{m}} = P_{in} v_{in} \ln \left(\frac{P_{out}}{P_{in}} \right)} \quad (13)$$

Isentropic Ideal Gas, Compression/Expansion

Isentropic implies a reversible and adiabatic process where $s = \text{constant}$. With an ideal gas, $Pv^k = \text{constant}$ and $(Pv^k)_{in} = (Pv^k)_{out}$.

Equation (8) becomes

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v dP = \int_{in}^{out} \left[\frac{(Pv^k)_{in}}{P} \right]^{1/k} dP$$


$$\boxed{\frac{\dot{W}}{\dot{m}} = \left(\frac{k}{k-1}\right) (Pv)_{in} \left[\left(\frac{P_{out}}{P_{in}}\right)^{(k-1)/k} - 1 \right] = c_p(T_{out} - T_{in})} \quad (14)$$

The right side of Eq. (14) is based on the fact that $\Delta KE + \Delta PE = 0$ and $dh = du + dPv$ and $du = 0$. Which leads to $h = \int v dP$.

Note: for the same inlet state and pressure ratio

$$\Rightarrow \left(\frac{\dot{W}}{\dot{m}}\right)_{rev.,isothermal} < \left(\frac{\dot{W}}{\dot{m}}\right)_{rev.,adiabatic}$$

Review of First and Second Law of Thermodynamics

	Reading	Problems
	2-6, 4-1, 4-2	4-27, 4-40, 4-41
	5-1 → 5-3	
	6-1, 6-2, 7-13	

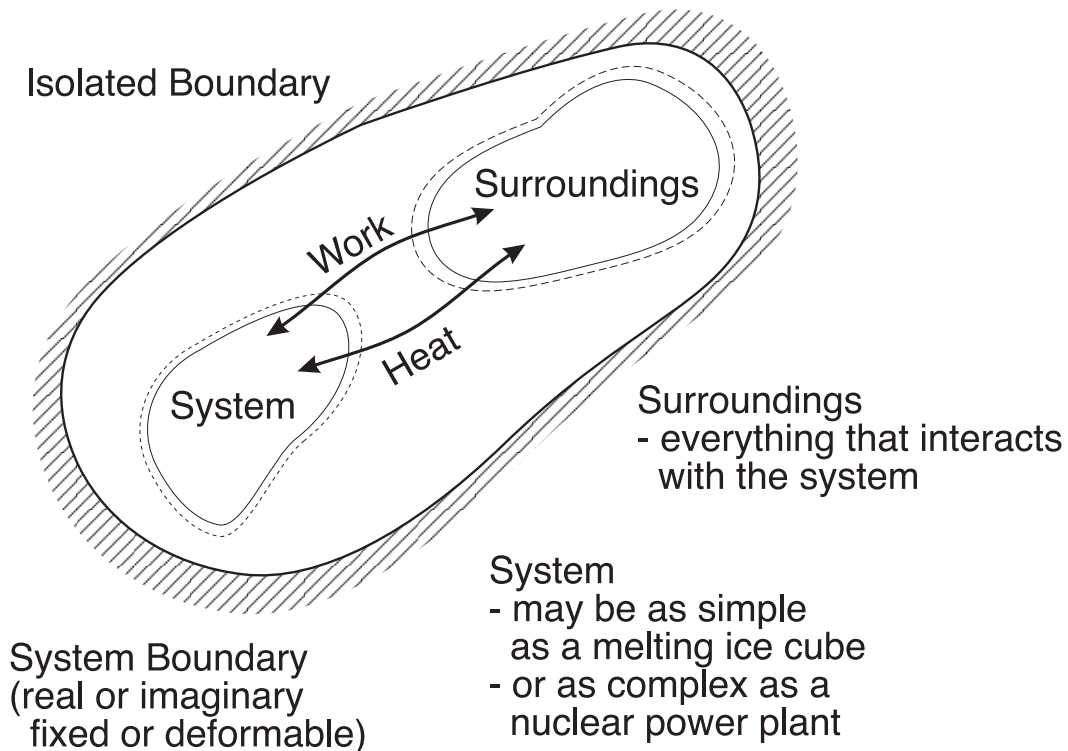
Definitions

SYSTEM:

- any specified collection of matter under study.
- all systems possess properties like mass, energy, entropy, volume, pressure, temperature, etc.

WORK & HEAT TRANSFER:

- thermodynamics deals with these properties of matter as a system interacts with its surroundings through work and heat transfer
- work and heat transfer are NOT properties → they are the forms that energy takes to cross the system boundary



First Law of Thermodynamics

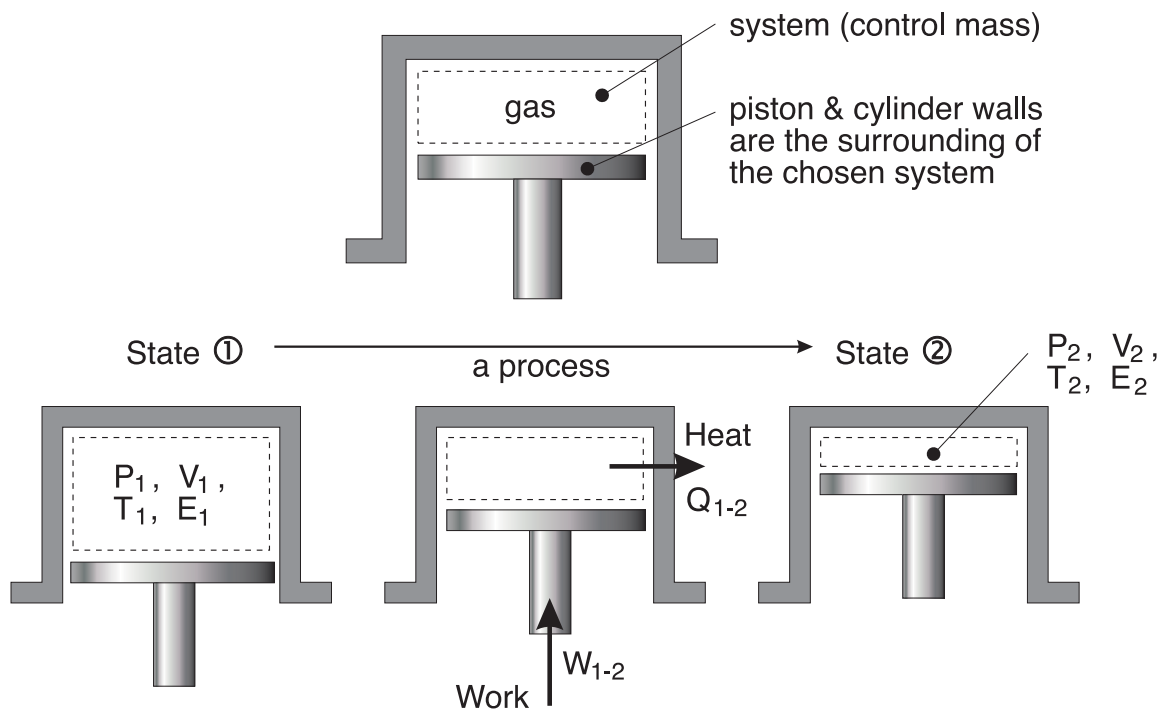
Control Mass (Closed System)

CONSERVATION OF ENERGY:

- the energy content of an isolated system is constant

energy entering – energy leaving = change of energy within the system

Example: A Gas Compressor



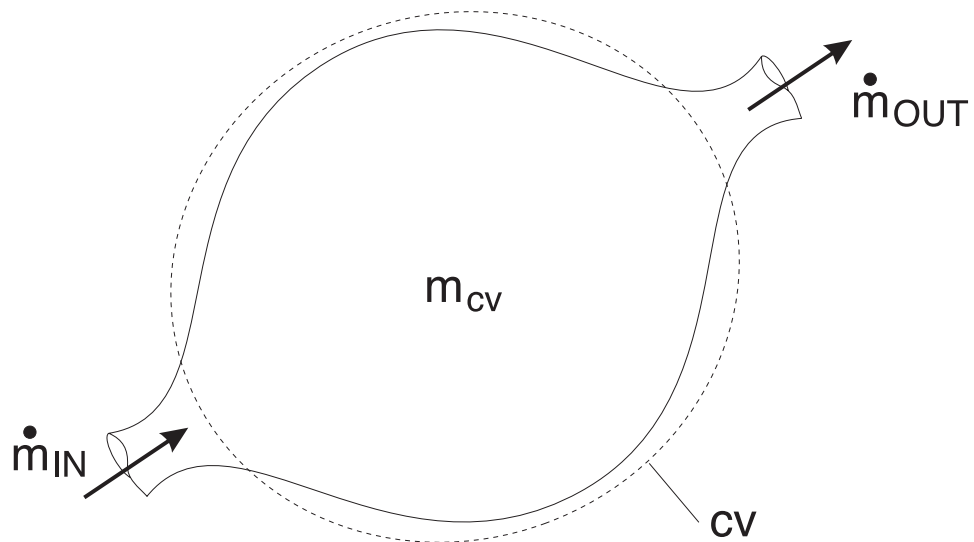
Performing a 1st law energy balance:

$$\left\{ \begin{array}{l} \text{Initial} \\ \text{Energy} \\ E_1 \end{array} \right\} + \left\{ \begin{array}{l} \text{Energy gain } W_{1-2} \\ \text{Energy loss } Q_{1-2} \end{array} \right\} = \left\{ \begin{array}{l} \text{Final} \\ \text{Energy} \\ E_2 \end{array} \right\}$$

$$\boxed{E_1 + W_{1-2} - Q_{1-2} = E_2}$$

Control Volume Analysis (Open System)

CONSERVATION OF MASS:



$$\left\{ \begin{array}{l} \text{rate of increase} \\ \text{of mass within} \\ \text{the CV} \end{array} \right\} = \left\{ \begin{array}{l} \text{net rate of} \\ \text{mass flow} \\ \text{IN} \end{array} \right\} - \left\{ \begin{array}{l} \text{net rate of} \\ \text{mass flow} \\ \text{OUT} \end{array} \right\}$$

$$\frac{d}{dt}(m_{CV}) = \dot{m}_{IN} - \dot{m}_{OUT}$$

where:

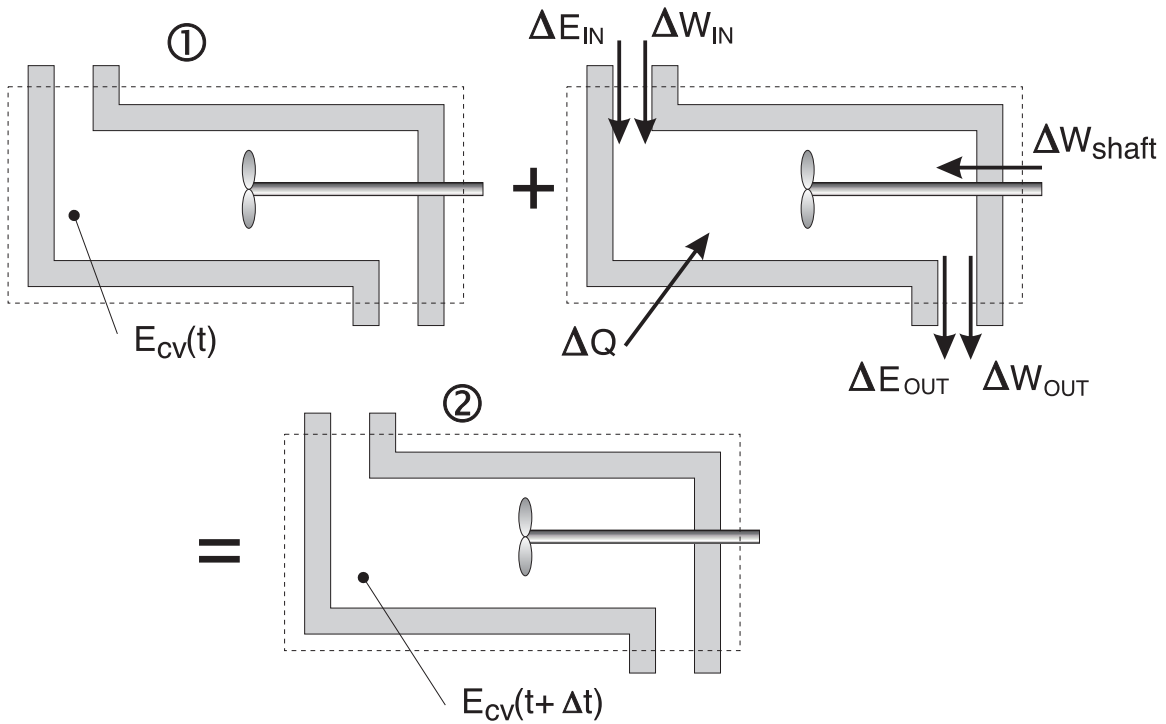
$$m_{CV} = \int_V \rho dV$$

$$\dot{m}_{IN} = (\rho v^* A)_{IN}$$

$$\dot{m}_{OUT} = (\rho v^* A)_{OUT}$$

with $v^* =$ average velocity

CONSERVATION OF ENERGY:



The 1st law states:

$$E_{CV}(t) + \Delta Q + \Delta W_{shaft} + (\Delta E_{IN} - \Delta E_{OUT}) + (\Delta W_{IN} - \Delta W_{OUT}) = E_{CV}(t + \Delta t) \quad (1)$$

where:

$$\Delta E_{IN} = e_{IN} \Delta m_{IN}$$

$$\Delta E_{OUT} = e_{OUT} \Delta m_{OUT}$$

$$\Delta W = \text{flow work}$$

$$e = \frac{E}{m} = \underbrace{u}_{\text{internal}} + \underbrace{\frac{(v^*)^2}{2}}_{\text{kinetic}} + \underbrace{gz}_{\text{potential}}$$

Second Law of Thermodynamics

Fundamentals

1. Like mass and energy, every system has entropy.

Entropy is a measure of the degree of microscopic disorder and represents our uncertainty about the microscopic state.

2. Unlike mass and energy, entropy can be produced but it can never be destroyed. That is, the entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

$$\mathcal{P}_m = m_2 - m_1 = 0 \text{ (conservation of mass)}$$

$$\mathcal{P}_E = E_2 - E_1 = 0 \text{ (conservation of energy)} \rightarrow \text{1st law}$$

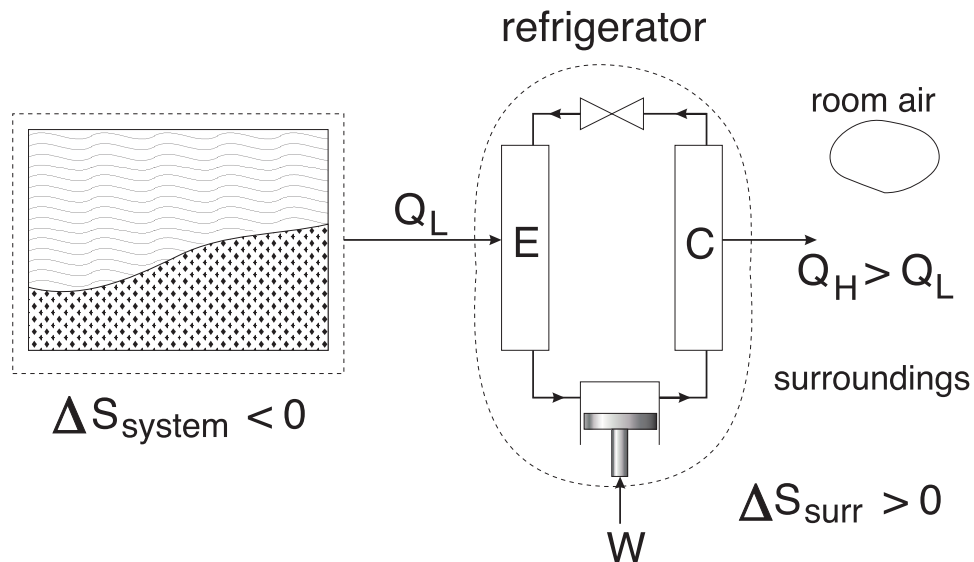
$$\mathcal{P}_S = S_2 - S_1 \geq 0 \rightarrow \text{2nd law}$$

The second law states:

$$(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0$$

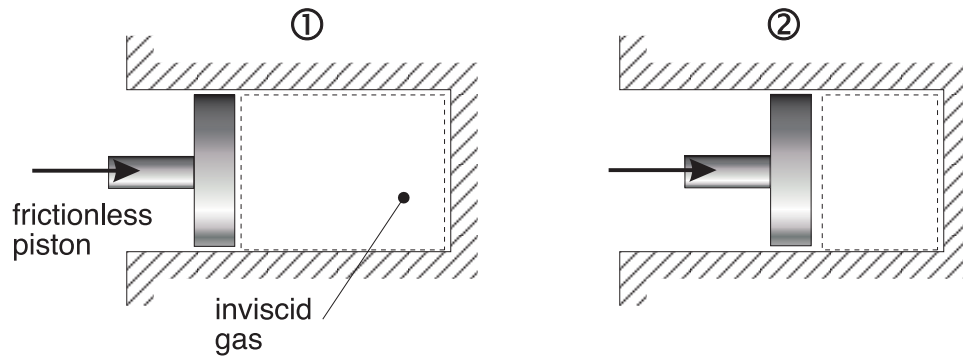
where $\Delta \equiv \text{final} - \text{initial}$

Example: A freezing process



3. **Reference:** In a perfect crystal of a pure substance at $T = 0 \text{ K}$, the molecules are completely motionless and are stacked precisely in accordance with the crystal structure. Since entropy is a measure of microscopic disorder, then in this case $S = 0$. That is, there is no uncertainty about the microscopic state.
4. **Relationship to Work:** For a given system, an increase in the microscopic disorder (that is an increase in entropy) results in a loss of ability to do useful work.
5. **Heat:** Energy transfer as heat takes place as work at the microscopic level but in a random, disorganized way. This type of energy transfer carries with it some chaos and thus results in entropy flow in or out of the system.
6. **Work:** Energy transfer by work is microscopically organized and therefore entropy-free.

Example: Slow adiabatic compression of a gas



Idealization - which makes the process completely reversible

A process $1 \rightarrow 2$ is said to be reversible if the reverse process $2 \rightarrow 1$ restores the system to its original state without leaving any change in either the system or its surroundings.

\rightarrow idealization where $S_2 = S_1 \Rightarrow \mathcal{P}_S = 0$

$T_2 > T_1 \Rightarrow$ increased microscopic disorder

$V_2 < V_1 \Rightarrow$ reduced uncertainty about the whereabouts of molecules

$$\underbrace{\text{Reversible}}_{\mathcal{P}_S=0} + \underbrace{\text{Adiabatic Process}}_{Q=0} \Rightarrow \underbrace{\text{Isentropic Process}}_{S_1=S_2}$$

The 2nd law states:

$$\mathcal{P}_S = (\Delta S)_{system} + (\Delta S)_{surr} \geq 0$$

where:

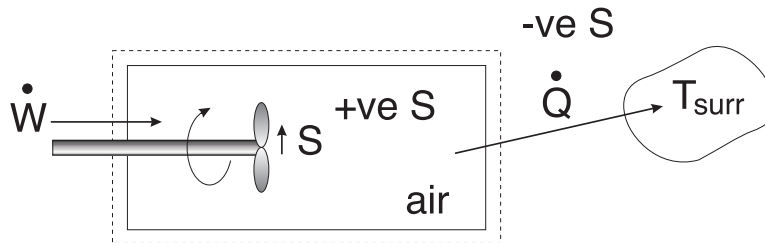
> 0 irreversible (real world)

$= 0$ reversible (frictionless, perfectly elastic, inviscid fluid)

But does:

Isentropic Process \Rightarrow *Reversible* + *Adiabatic*

NOT ALWAYS - the entropy increase of a substance during a process as a result of irreversibilities may be offset by a decrease in entropy as a result of heat losses.



General Derivation of Gibb's Equation

From a 1st law energy balance when KE and PE are neglected

Energy Input = *Energy Output* + *Increase in Energy Storage*

$$\underbrace{\frac{dQ}{amount}} = dW + \underbrace{\frac{dU}{differential}} \quad (1)$$

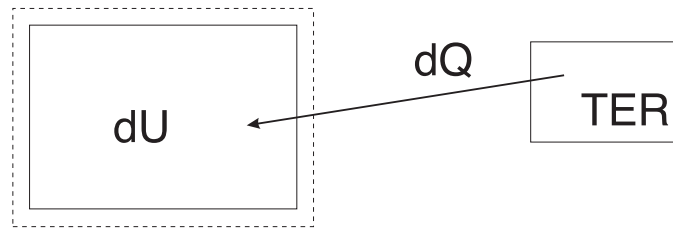
We know that the differential form of entropy is

$$dS = \frac{dQ}{T} \quad (2) \quad dW = PdV \quad (3)$$

Combining Eqs. 1, 2 and 3

$$dS = \frac{dU}{T} + \frac{PdV}{T} \Rightarrow \underbrace{ds = \frac{du}{T} + \frac{Pdv}{T}}_{\text{per unit mass}}$$

Second Law Analysis for a Control Mass



- control mass is uniformly at T_{TER} at all times
- control mass has a fixed size ($V = \text{constant}$)

From Gibb's equation

$$T_{TER} dS = dU + P dV^0$$

From the 1st law

$$dU = dQ$$

Therefore for a reversible process

$$dS = \frac{dQ}{T_{TER}}$$

We integrate to give

$$S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}}$$

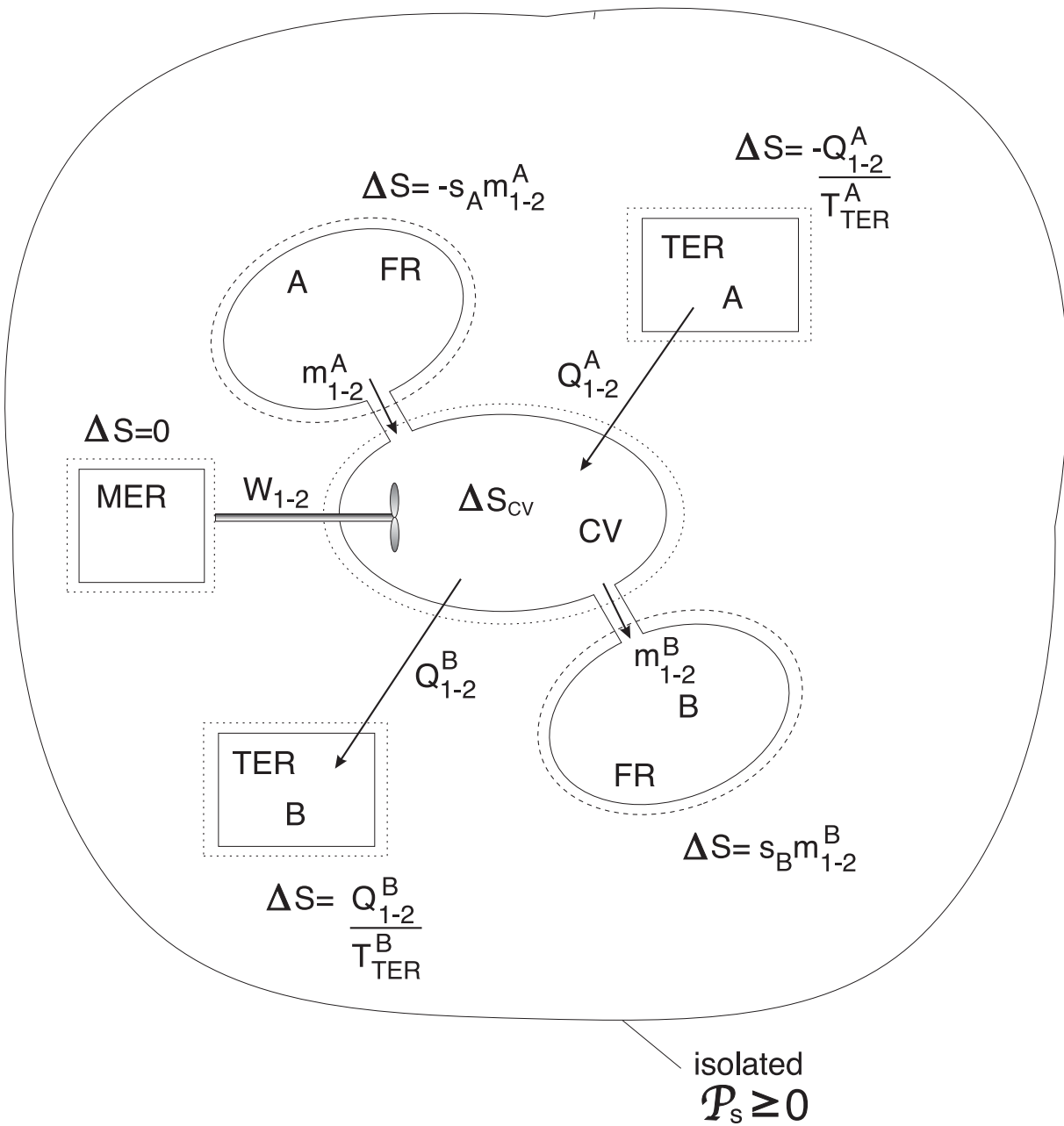
and for a non-reversible process

$$dS = \frac{dQ}{T_{TER}} + d\mathcal{P}_S$$

We integrate to give

$$S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}} + \mathcal{P}_{S_{1-2}}$$

Second Law Analysis for a Control Volume



where:

- FR - fluid reservoir
- TER - thermal energy reservoir
- MER - mechanical energy reservoir

For the isolated system

$$(\Delta S)_{sys} + (\Delta S)_{sur} = \mathcal{P}_{S_{1-2}} \geq 0$$

$$\Delta S_{CV} - s_A m_{1-2}^A + s_B m_{1-2}^B - \frac{Q_{1-2}^A}{T_{TER}^A} + \frac{Q_{1-2}^B}{T_{TER}^B} = \mathcal{P}_{S_{1-2}}$$


or as a rate equation

$$\left(\frac{dS}{dt}\right)_{CV} = \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{IN} - \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{OUT} + \dot{\mathcal{P}}_S$$

This can be thought of as

$$\textit{accumulation} = \textit{IN} - \textit{OUT} + \textit{generation}$$

Availability

	Reading	Problems
	8-1 → 8-8	8-29, 8-34, 8-50, 8-53, 8-63 8-71, 8-93, 8-103, 8-118, 8-137

Second Law Analysis of Systems

AVAILABILITY:

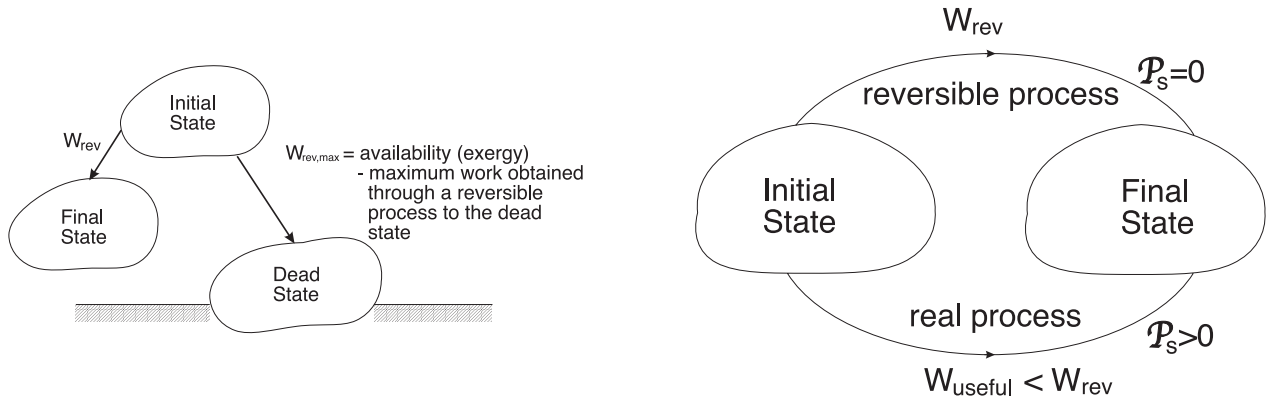
- the theoretical maximum amount of work that can be obtained from a system at a given state P_1 and T_1 when interacting with a reference atmosphere at the constant pressure and temperature P_0 and T_0 .
- describes the work potential of a given system.
- also referred to as “exergy”.

The following observations can be made about availability:

1. Availability is a **property** - since any quantity that is fixed when the state is fixed is a property. For a system at state 1 and specified values of the atmosphere of T_0 and P_0 , the maximum useful work that can be produced is fixed.
2. Availability is a **composite property** - since its value depends upon an external datum - the temperature and pressure of the dead state.
3. Availability of a system is 0 at its **dead state** when $T = T_0$ and $P = P_0$. It is not possible for the system to interact with the reference atmosphere at the dead state. The system is said to be in thermodynamic equilibrium with its surroundings.
4. Unless otherwise stated, assume the dead state to be:

$$P_0 = 1 \text{ atm}$$

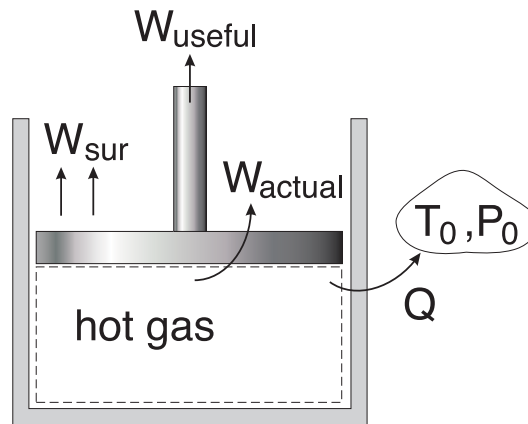
$$T_0 = 25^\circ\text{C}$$



5. The maximum work is obtained through a reversible process to the dead state.

$$\underbrace{REVERSIBLE\ WORK}_{W_{rev}} = \underbrace{USEFUL\ WORK}_{W_{useful}} + \underbrace{IRREVERSIBILITY}_{I}$$

Control Mass Analysis



- we know

$$W_{rev} = W_{useful} + I$$

but as shown in the figure, the actual work of the process is divided into two components

$$W_{actual} = W_{useful} + W_{sur}$$

- where W_{sur} is the part of the work done against the surroundings to displace the ambient air

$$W_{sur} = P_0(V_2 - V_1) = -P_0(V_1 - V_2)$$

- this is unavoidable \rightarrow this is not useful work. Nothing is gained by pushing the atmosphere away.

To find W_{actual} , from the 1st law

$$E_1 - Q - W_{actual} = E_2 \quad \rightarrow \quad Q = E_1 - E_2 - W_{actual}$$

From the 2nd law

$$\begin{aligned} \mathcal{P}_s &= \Delta S_{system} + \Delta S_{sur} \geq 0 \\ &= S_2 - S_1 + \frac{Q}{T_0} \end{aligned}$$

But from the 1st law balance we know

$$\frac{Q}{T_0} = \frac{E_1 - E_2 - W_{actual}}{T_0}$$

and when we combine this with the 2nd law

$$\mathcal{P}_s = S_2 - S_1 + \frac{E_1 - E_2 - W_{actual}}{T_0}$$

which leads to

$$W_{actual} = (E_1 - E_2) + T_0(S_2 - S_1) - T_0\mathcal{P}_s$$

or by reversing the order of S_2 and S_1

$$W_{actual} = (E_1 - E_2) - T_0(S_1 - S_2) - T_0\mathcal{P}_s$$

But we also know that

$$W_{useful} = W_{actual} - W_{sur}$$

therefore

$$W_{useful} = (E_1 - E_2) - T_0(S_1 - S_2) + \underbrace{P_0(V_1 - V_2)}_{-W_{sur}} - T_0\mathcal{P}_s$$

and

$$\begin{aligned} W_{rev} &= W_{useful} + I \\ &= W_{actual} - W_{sur} + I \end{aligned}$$

where

$$I = T_0\mathcal{P}_s$$

Therefore

$$W_{rev} = (E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2)$$

In summary

$W_{actual} = (E_1 - E_2) - T_0(S_1 - S_2) - T_0\mathcal{P}_s$ $W_{useful} = (E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2) - T_0\mathcal{P}_s$ $X = \Phi = W_{rev} = (E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2)$

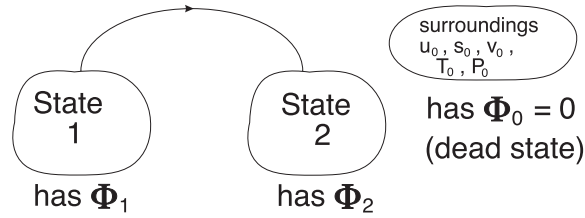
Define

$$\begin{aligned} X = \Phi &= \text{CONTROL MASS AVAILABILITY} \\ &= W_{rev} \text{ (in going to the dead state)} \\ &= (E - E_0) - T_0(S - S_0) + P_0(V - V_0) \end{aligned}$$

where the specific availability is defined as

$$\phi = \frac{\Phi}{m}$$

What is the availability in going from one state to another?



The reversible work is

$$W_{rev} = (\Phi_1 - \Phi_0) - (\Phi_2 - \Phi_0) = \Phi_1 - \Phi_2$$

but we also know

$$\Phi_1 = (E_1 - E_0) - T_0(S_1 - S_0) + P_0(V_1 - V_0)$$

$$\Phi_2 = (E_2 - E_0) - T_0(S_2 - S_0) + P_0(V_2 - V_0)$$

$$\Phi_1 - \Phi_2 = (E_1 - E_2) - T_0(S_1 - S_2) + P_0(V_1 - V_2)$$

The availability destroyed is

$$X_{des} = I = W_{rev} - W_{useful} = T_0 \mathcal{P}_s = T_0 S_{gen}$$

This can be referred to as: irreversibilities, availability destruction or loss of availability.

Control Volume Analysis

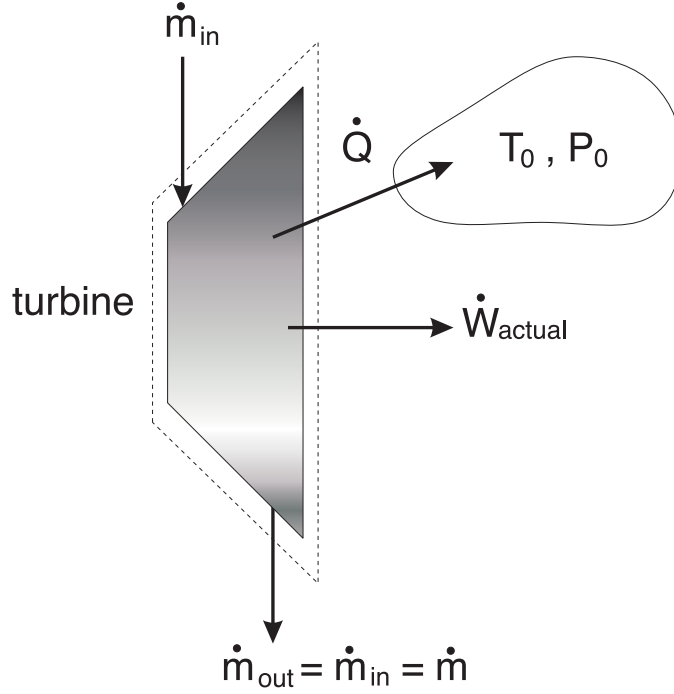
Consider a steady state, steady flow (SS-SF) process

From the 1st law

$$\frac{dE_{cv}}{dt} = -\dot{W}_{actual} - \dot{Q} + \left[\dot{m} \left(h + \frac{(v^*)^2}{2} + gz \right) \right]_{in} - \left[\dot{m} \left(h + \frac{(v^*)^2}{2} + gz \right) \right]_{out} \quad (1)$$

From the 2nd law

$$\frac{dS_{cv}}{dt} = \left(\dot{m}s + \frac{\dot{Q}^{*0}}{T_{TER}} \right)_{in} - \left(\dot{m}s + \frac{\dot{Q}}{T_0} \right)_{out} + \dot{\mathcal{P}}_s \quad (2)$$



Combining (1) and (2) through the \dot{Q} term, leads to the actual work output of the turbine, given as

$$\begin{aligned}\dot{W}_{actual} &= \left[\dot{m} \left(h + \frac{(v^*)^2}{2} + gz - T_0 s \right) \right]_{in} - \left[\dot{m} \left(h + \frac{(v^*)^2}{2} + gz - T_0 s \right) \right]_{out} - T_0 \dot{\mathcal{P}}_s \\ &= \dot{m} [-T_0 \Delta s + \Delta h + \Delta KE + \Delta PE] - (T_0 \dot{\mathcal{P}}_s) \quad (3)\end{aligned}$$

\dot{W}_{actual} is the actual work output of the turbine.

The specific flow availability, ψ , is given as

$$\psi = -T_0(s - s_0) + (h - h_0) + \left(\frac{(v^*)^2}{2} - \frac{(v_0^*)^2}{2} \right) + g(z - z_0) \quad (4)$$

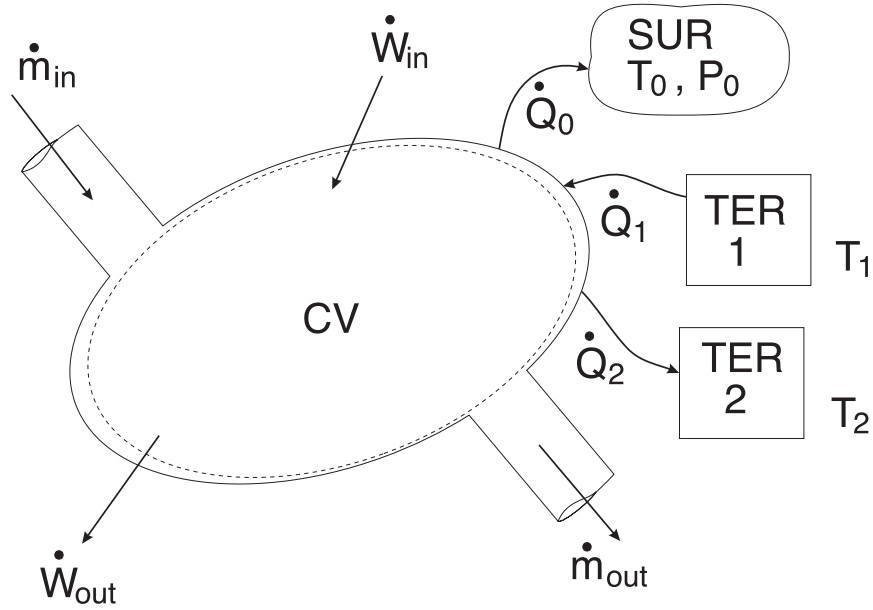
For a steady state, steady flow process where we assume KE=PE=0

$$\dot{W}_{rev} = (\dot{m}\psi)_{in} - (\dot{m}\psi)_{out} \quad (5)$$

$$\dot{X}_{des} = \dot{I} = \dot{W}_{rev} - \dot{W}_{actual} = T_0 \dot{\mathcal{P}}_s = T_0 \dot{S}_{gen} \quad (6)$$

$$\psi = (h - h_0) - T_0(s - s_0) \quad (7)$$

The General Exergy Equation



From the 1st law

$$\frac{dE_{cv}}{dt} = \dot{W}_{in} - \dot{W}_{out} - \dot{Q}_0 + \dot{Q}_1 - \dot{Q}_2 + [\dot{m}(e + Pv)]_{in} - [\dot{m}(e + Pv)]_{out} \quad (1)$$

From the 2nd law

$$\frac{dS_{cv}}{dt} = \left(\dot{m}s - \frac{\dot{Q}_0}{T_0} + \frac{\dot{Q}_1}{T_1} \right)_{in} - \left(\dot{m}s + \frac{\dot{Q}_2}{T_2} \right)_{out} + \dot{\mathcal{P}}_s \quad (2)$$

Multiply (2) by T_0 and subtract from (1) to eliminate \dot{Q}_0 , which leads to the generalized exergy equation

$$\begin{aligned} \frac{d}{dt}(E - T_0S)_{CV} = & \dot{W}_{in} - \dot{W}_{out} + [\dot{m}(e + Pv - T_0s)]_{in} \\ & [\dot{m}(e + Pv - T_0s)]_{out} + \left(\dot{Q}_1 - \frac{T_0\dot{Q}_1}{T_1} \right)_{in} \\ & - \left(\dot{Q}_2 - \frac{T_0\dot{Q}_2}{T_2} \right)_{out} - T_0\dot{\mathcal{P}}_s \quad (3) \end{aligned}$$

We can rewrite Eq. (3) in a generalized form by introducing the definitions of Φ and ψ .

$$\begin{aligned} \frac{d\Phi}{dt} = & P_0 \frac{dV_{CV}}{dt} + \left[\dot{W} + \dot{m}\psi + \dot{Q} \left(1 - \frac{T_0}{T_{TER}} \right) \right]_{in} \\ & - \left[\dot{W} + \dot{m}\psi + \dot{Q} \left(1 - \frac{T_0}{T_{TER}} \right) \right]_{out} - \dot{I} \end{aligned}$$

where

$$\begin{aligned} \dot{I} = \dot{X}_{des} &= T_0 \dot{\mathcal{P}}_s \\ &= \textit{exergy destruction rate} \\ \Phi &= [(E - E_0) + P_0(V - V_0) - T_0(S - S_0)] \\ &= \textit{non - flow exergy} \\ \psi &= (h - h_0) - T_0(s - s_0) + \frac{1}{2} [(v^*)^2 - (v_0^*)^2] + g(z - z_0) \\ &= \textit{flow exergy} \\ \dot{W}_{useful} &= \underbrace{(\dot{W}_{in} - \dot{W}_{out})}_{\dot{W}_{actual}} - \underbrace{\left(P_0 \frac{dV_{CV}}{dt} \right)}_{W_{sur}} \end{aligned}$$

Aside: The left side of the above equation is

$$\frac{d\Phi}{dt} = \frac{dE + P_0 dV - T_0 dS}{dt}$$

but the left side of Eq. (3) does not contain the term $P_0 dV$. Therefore, we must add a term $P_0 dV$ to both the left and right side of the above equation in order to preserve a balance. Hence the term

$$P_0 \frac{dV}{dt}$$

appears on the right side of the above equation to preserve this balance, while the left side is

$$\frac{d\Phi}{dt} = \frac{(dE + P_0 dV - T_0 dS)}{dt}$$

Efficiency and Effectiveness

1. First law efficiency (thermal efficiency)

$$\eta = \frac{\text{net work output}}{\text{gross heat input}} = \frac{W_{net}}{Q_{in}}$$

Carnot cycle

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

2. Second Law Efficiency (effectiveness)

$$\eta_{2nd} = \frac{\text{net work output}}{\text{maximum reversible work}} = \frac{\text{net work output}}{\text{availability}}$$

$$\text{Turbine} \rightarrow \eta_{2nd} = \frac{\dot{W}/\dot{m}}{\psi_e - \psi_i}$$

$$\text{Compressor} \rightarrow \eta_{2nd} = \frac{\psi_e - \psi_i}{\dot{W}/\dot{m}}$$

$$\text{Heat Source} \rightarrow \eta_{2nd} = \frac{\dot{W}/\dot{m}}{\dot{Q}/\dot{m} \left[1 - \frac{T_0}{T_{TER}} \right]}$$

3. Isentropic efficiency (process efficiency)


(a) adiabatic turbine efficiency

$$\eta_T = \frac{\text{work of actual adiabatic expansion}}{\text{work of reversible adiabatic expansion}} = \frac{W_{act}}{W_S}$$

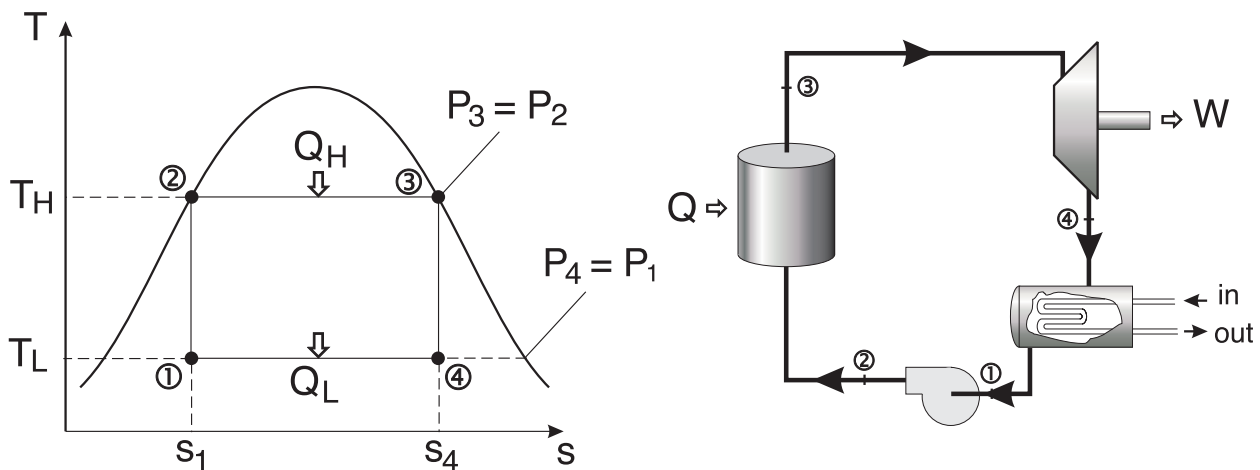
(b) adiabatic compressor efficiency

$$\eta_C = \frac{\text{work of reversible adiabatic compression}}{\text{work of actual adiabatic compression}} = \frac{W_S}{W_{act}}$$

Carnot Cycle

	<p>Reading 6-7, 6-8, 6-10, 9-2, 10-1</p>	<p>Problems</p>
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- an ideal theoretical cycle that is the most efficient conceivable
- based on a fully reversible heat engine - it does not include any of the irreversibilities associated with friction, viscous flow, etc.
- in practice the thermal efficiency of real world heat engines are about half that of the ideal, Carnot cycle



Process	State Points	Description
Pump	1 → 2	isentropic compression from $T_L \rightarrow T_H$ to return vapour to a liquid state
Heat Supply	2 → 3	heat is supplied at constant temperature and pressure
Work Output	3 → 4	the vapour expands isentropically from the high pressure and temperature to the low pressure
Condenser	4 → 1	the vapour which is wet at 4 has to be cooled to state point 1

Cycle Efficiency

- defined as the net work output divided by the gross heat supplied

$$\begin{aligned}\eta &= \frac{W_{net}}{Q_H} \\ &= \frac{Q_H - Q_L}{Q_H} \\ &= 1 - \frac{T_L}{T_H}\end{aligned}$$

From the figure the gross heat supplied is

$$Q_H = \text{area}(s_1 \rightarrow s_4 \rightarrow 3 \rightarrow 2 \rightarrow s_1) = T_H(s_4 - s_1)$$

The net work output is

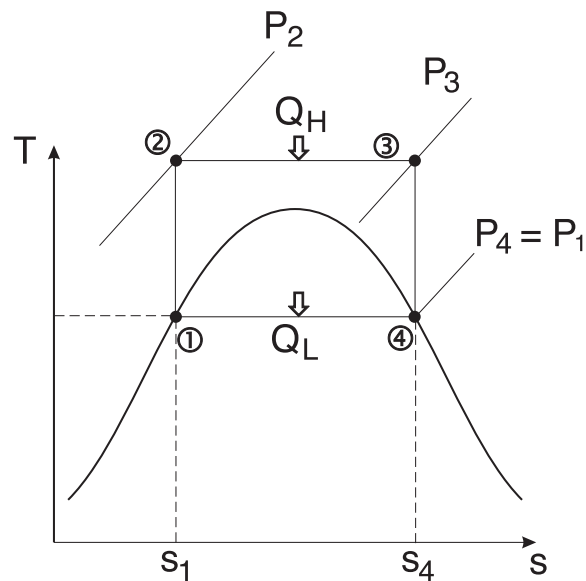
$$Q_H - Q_L = \text{area}(1 \rightarrow 4 \rightarrow 3 \rightarrow 2) = (T_H - T_L)(s_4 - s_1)$$

Therefore the Carnot efficiency is

$$\eta = \frac{(T_H - T_L)(s_4 - s_1)}{T_H(s_4 - s_1)} = 1 - \frac{T_L}{T_H}$$

Practical Problems


- at state point 1 the steam is wet at T_L and it is difficult to pump water/steam (two phase) to state point 2
- the pump can be sized smaller if the fluid is 100% liquid water
- the pump is smaller, cheaper and more efficient
- can we devise a Carnot cycle to operate outside the wet vapour region



- between state points 2 and 3 the vapour must be isothermal and at different pressures - this is difficult to achieve
- the high temperature and pressure at 2 and 3 present metallurgical limitations

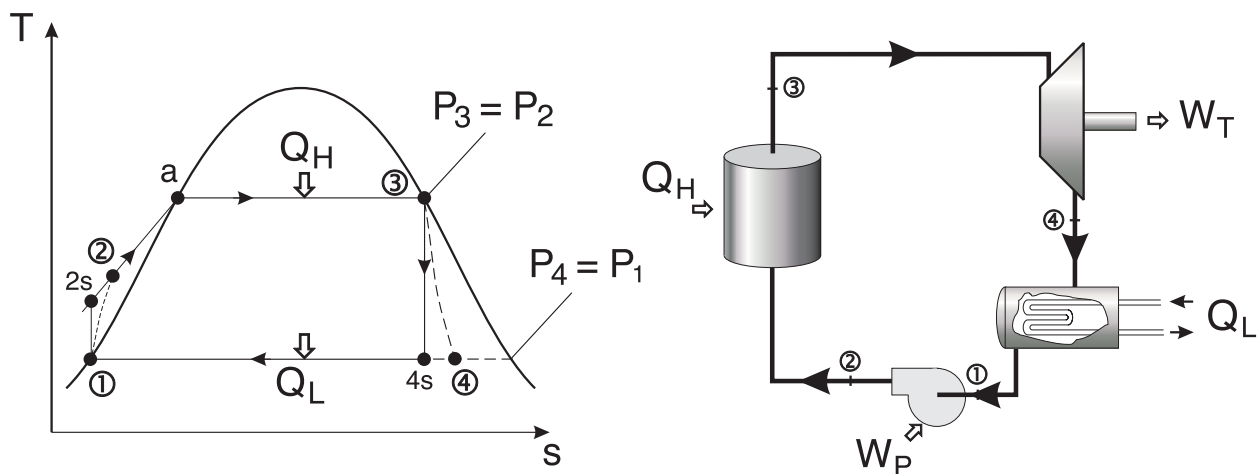
The net effect is that the Carnot cycle is not feasible for steam power plants.

Rankine Cycle

	Reading	Problems
	10-2 → 10-7	10-16, 10-34, 10-37, 10-44, 10-47, 10-59

Definitions

- working fluid is alternately vaporized and condensed as it recirculates in a closed cycle
- water is typically used as the working fluid because of its low cost and relatively large value of enthalpy of vaporization
- the standard vapour cycle that excludes internal irreversibilities is called the **Ideal Rankine Cycle**



- the condensation process is allowed to proceed to completion between state points 4 → 1
 - provides a saturated liquid at 1
- the water at state point 1 can be conveniently pumped to the boiler pressure at state point 2
- but the water is not at the saturation temperature corresponding to the boiler pressure
- heat must be added to change the water at 2 to saturated water at 'a'
- when heat is added at non-constant temperature (between 2 – a), the cycle efficiency will decrease

Analyze the Process

Assume steady flow, $KE = PE = 0$.

From a 1st law balance, we know

$$\textit{energy in} = \textit{energy out}$$

Device	1st Law Balance
Boiler	$h_2 + q_H = h_3 \Rightarrow q_H = h_3 - h_2$ (in)
Turbine	$h_3 = h_4 + w_T \Rightarrow w_T = h_3 - h_4$ (out)
Condenser	$h_4 = h_1 + q_L \Rightarrow q_L = h_4 - h_1$ (out)
Pump	$h_1 + w_P = h_2 \Rightarrow w_P = h_2 - h_1$ (in)

The net work output is given as

$$\begin{aligned}w_T - w_p &= (h_3 - h_4) - (h_2 - h_1) \\ &= (h_3 - h_4) + (h_1 - h_2)\end{aligned}$$

The net heat supplied to the boiler is

$$q_H = (h_3 - h_2)$$

The Rankine efficiency is

$$\begin{aligned}\eta_R &= \frac{\textit{net work output}}{\textit{heat supplied to the boiler}} \\ &= \frac{(h_3 - h_4) + (h_1 - h_2)}{(h_3 - h_2)}\end{aligned}$$

If we consider the fluid to be incompressible

$$(h_2 - h_1) = v(P_2 - P_1)$$

Since the actual process is irreversible, an isentropic efficiency can be defined such that

$$\text{Expansion process} \Rightarrow \text{Isentropic efficiency} = \frac{\text{actual work}}{\text{isentropic work}}$$

$$\text{Compression process} \Rightarrow \text{Isentropic efficiency} = \frac{\text{isentropic work}}{\text{actual work}}$$

Both isentropic efficiencies will have a numerical value between 0 and 1.

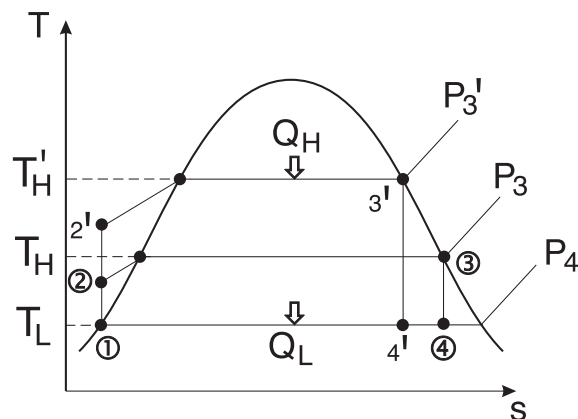
Effects of Boiler and Condenser Pressure

We know the efficiency is proportional to

$$\eta \propto 1 - \frac{T_L}{T_H}$$

The question is \rightarrow how do we increase efficiency $\Rightarrow T_L \downarrow$ and/or $T_H \uparrow$.

1. INCREASED BOILER PRESSURE:



- an increase in boiler pressure results in a higher T_H for the same T_L , therefore $\eta \uparrow$.
- but 4' has a lower quality than 4
 - wetter steam at the turbine exhaust

- results in cavitation of the turbine blades
- $\eta \downarrow$ plus \uparrow maintenance
- quality should be $> 80\%$ at the turbine exhaust

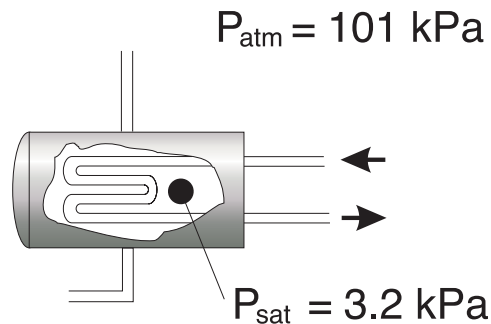
2. LOWER T_L :

- we are generally limited by the *TER* (lake, river, etc.)

eg. lake @ $15\text{ }^\circ\text{C}$ + $\underbrace{\Delta T = 10\text{ }^\circ\text{C}}_{\text{resistance to HT}} = 25\text{ }^\circ\text{C}$

$\Rightarrow P_{sat} = 3.2\text{ kPa}$.

- this is why we have a condenser
 - the pressure at the exit of the turbine can be less than atmospheric pressure
 - the closed loop of the condenser allows us to use treated water on the cycle side
 - but if the pressure is less than atmospheric pressure, air can leak into the condenser, preventing condensation



3. INCREASED T_H BY ADDING SUPERHEAT:

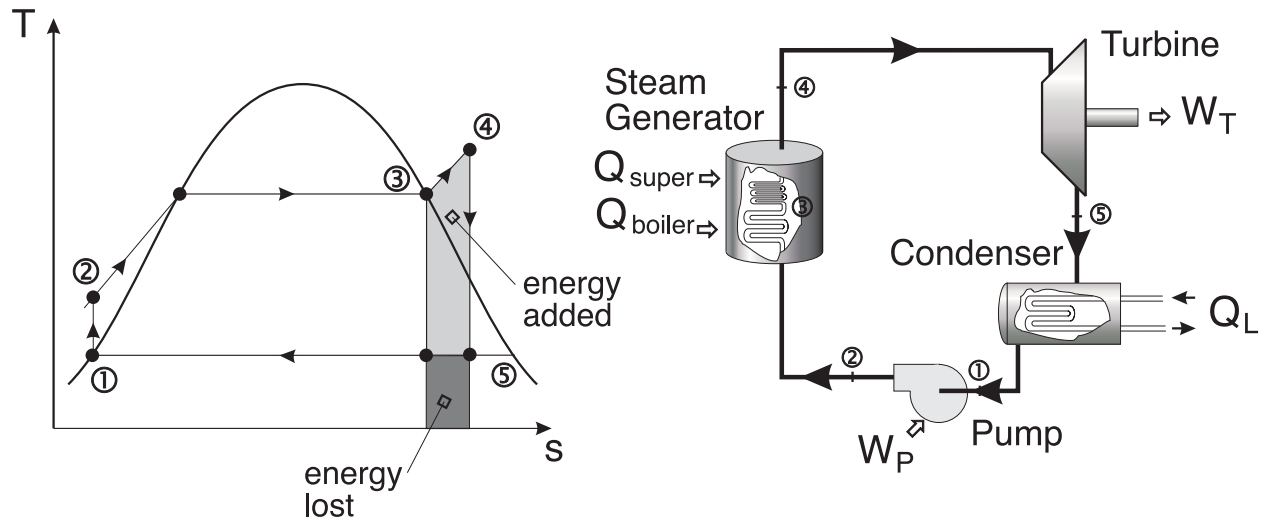
- the average temperature at which heat is supplied in the boiler can be increased by superheating the steam
 - dry saturated steam from the boiler is passed through a second bank of smaller bore tubes within the boiler until the steam reaches the required temperature

The advantage is

$$\eta = \frac{W_{net} \uparrow}{Q_H \uparrow} \quad \text{overall } \uparrow$$

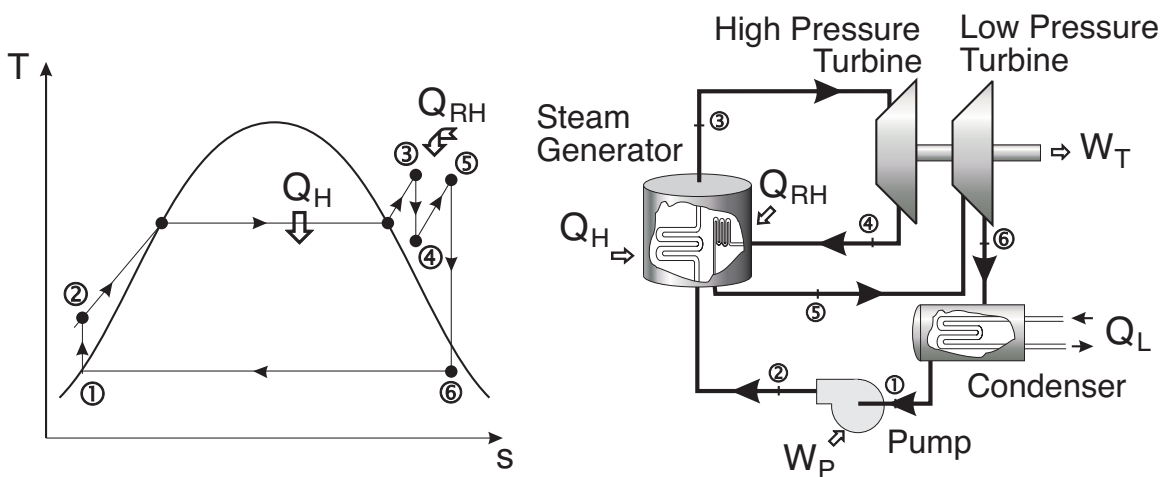
The value of \bar{T}_H , the mean temperature at which heat is added, increases, while \bar{T}_L remains constant. Therefore the efficiency increases.

- the quality of the turbine exhaust increases, hopefully where $x > 0.9$
- with sufficient superheating the turbine exhaust can fall in the superheated region.



Rankine Cycle with Reheat

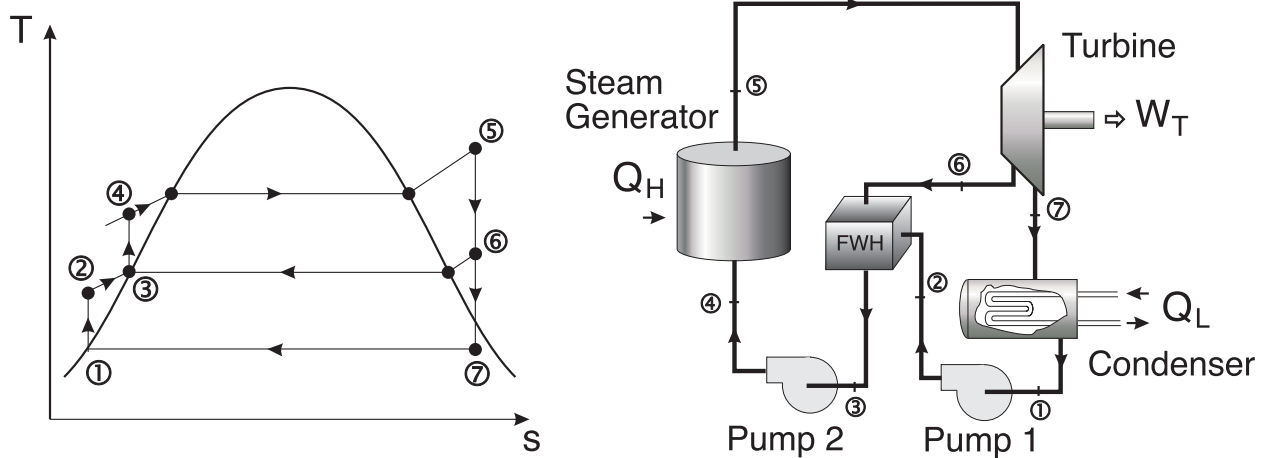
- the wetness at the exhaust of the turbine should be no greater than 10% - this can result in physical erosion of the turbine blades
- but high boiler pressures are required for high efficiency - tends to lead to a high wetness ratio
- to improve the exhaust steam conditions, the steam can be reheated with the expansion carried out in two steps



- the temperature of the steam entering the turbine is limited by metallurgical constraints
- modern boilers can handle up to 30 MPa and a maximum temperature of $T_{max} \approx 650 \text{ }^\circ\text{C}$.
- newer materials, such as ceramic blades can handle temperatures up to $750 \text{ }^\circ\text{C}$.

Rankine Cycle with Regeneration

- Carnot cycle has efficiency: $\eta = 1 - T_L/T_H$
 - add Q_H at as high a T_H as possible
 - reject Q_L at as low a T_L as possible
- the Rankine cycle can be used with a **Feedwater Heater** to heat the high pressure sub-cooled water at the pump exit to the saturation temperature
 - most of the heat addition (Q_H) is done at high temperature



Feedwater Heaters

There are two different types of feedwater heaters

1. **OPEN FWH:** the streams mix \rightarrow high temperature steam with low temperature water at constant pressure
2. **CLOSED FWH:** a heat exchanger is used to transfer heat between the two streams but the streams do *not* mix. The two streams can be maintained at different pressures.

1. OPEN FWH:

- working fluid passes isentropically through the turbine stages and pumps
- steam enters the first stage turbine at state 1 and expands to state 2 - where a fraction of the total flow is bled off into an open feedwater heater at P_2
- the rest of the steam expands into the second stage turbine at state point 3 - this portion of the fluid is condensed and pumped as a saturated liquid to the FWH at P_2
- a single mixed stream exists the FWH at state point 6

Analysis:

- we must determine the mass flow rates through each of the components.

By performing an mass balance over the turbine

$$\dot{m}_6 + \dot{m}_7 = \dot{m}_5 \quad (1)$$

If we normalize Eq. (1) with respect the total mass flow rate \dot{m}_1

$$\frac{\dot{m}_6}{\dot{m}_5} + \frac{\dot{m}_7}{\dot{m}_5} = 1 \quad (2)$$

Let the flow at state point 2 be

$$y = \frac{\dot{m}_6}{\dot{m}_5}$$

Therefore

$$\frac{\dot{m}_7}{\dot{m}_5} = 1 - y \quad (3)$$

Assuming no heat loss at the FWH, establish an energy balance across the FWH

$$yh_6 + (1 - y)h_2 = 1 \cdot h_3$$

$$y = \frac{h_3 - h_2}{h_6 - h_2} = \frac{\dot{m}_6}{\dot{m}_5}$$

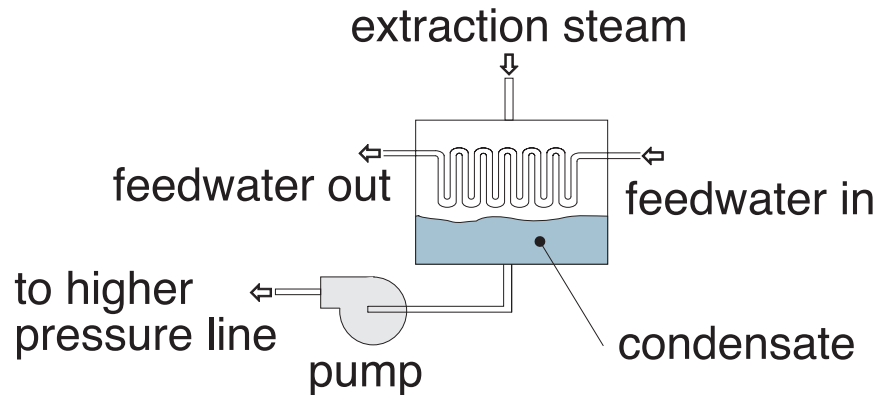
and

$$1 - y = \frac{\dot{m}_7}{\dot{m}_5}$$

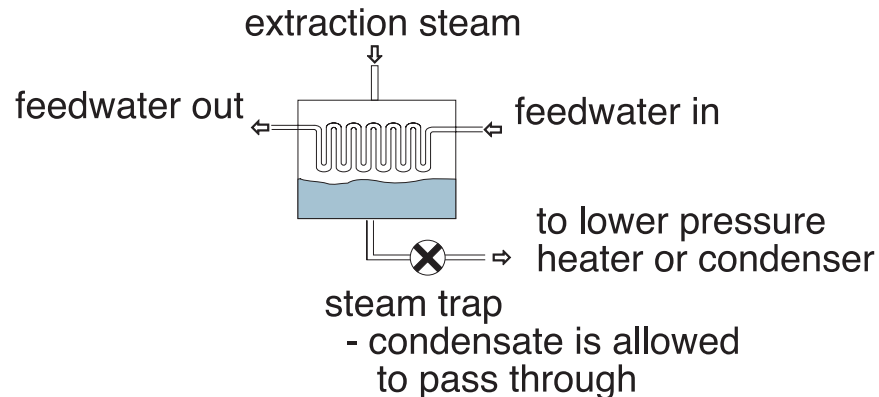
2. CLOSED FWH:

- two variations exist

(a) pump the condensate back to the high pressure line



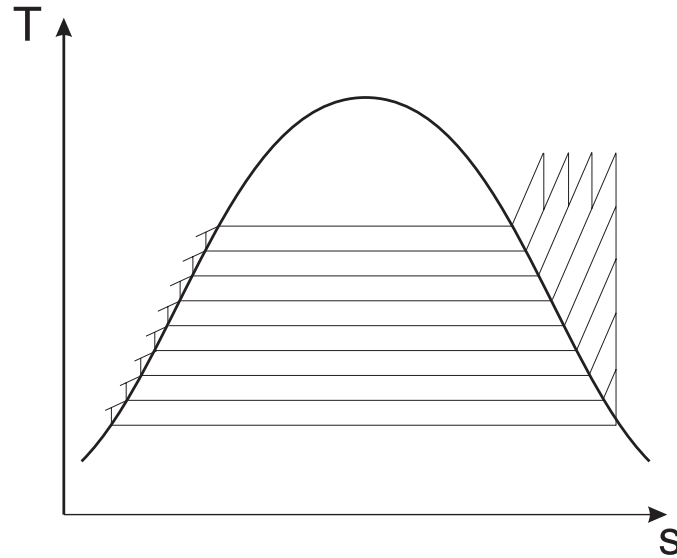
- (b) – a steam trap is inserted in the condensed steam line that allows only liquid to pass
- liquid is passed to a low pressure region such as the condenser or a low pressure heater



- the incoming feedwater does not mix with the extracted steam
 - both streams flow separately through the heater
 - the two streams can have different pressures

Other Topics

“IDEAL” RANKINE CYCLE:




- too expensive to build
- requires multiple reheat and regeneration cycles
- approaches Carnot efficiency

TOPPING CYCLE (BINARY CYCLE):

- involves two Rankine cycles running in tandem with different working fluids such as mercury and water
- why:
 - typically a boiler will supply energy at $1300 - 1400\text{ }^{\circ}\text{C}$
 - but $T_{critical}$ for water is $374.14\text{ }^{\circ}\text{C}$
 - * most energy is absorbed below this temperature
 - * high ΔT between the boiler source and the water leads to a major source of irreversibilities
 - $T_{critical}$ for mercury is about $1500\text{ }^{\circ}\text{C}$
 - * no need for superheating
 - combine the large enthalpy of evaporation of water at low temperatures with the advantages of mercury at high temperatures
 - in addition, the mercury dome leads to a high quality at the exit of the turbine

Refrigeration Cycle

	Reading	Problems
	11-1 → 11-7, 11-9	11-11, 11-44, 11-47, 11-104

Definitions

- a refrigeration system removes thermal energy from a low-temperature region and transfers heat to a high-temperature region.
- the 1st law of thermodynamics tells us that heat flow occurs from a hot source to a cooler sink, therefore, energy in the form of work must be added to the process to get heat to flow from a low temperature region to a hot temperature region.
- refrigeration cycles may be classified as
 - vapour compression
 - gas compression
- we will examine only the vapour compression systems
- refrigerators and heat pumps have a great deal in common. The primary difference is in the manner in which heat is utilized.

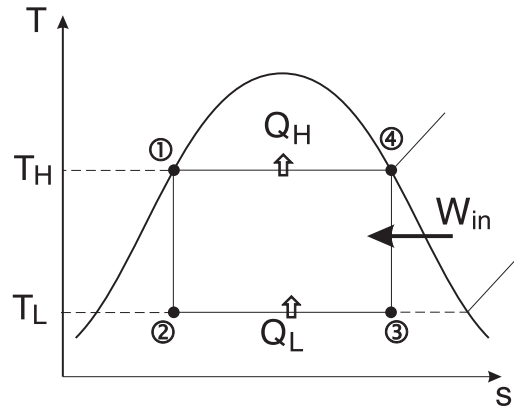
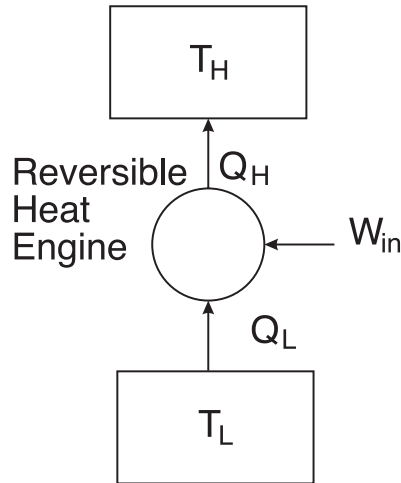
– **Refrigerator** $\downarrow C$ \rightarrow $\uparrow H$
 takes heat from transfers to

– **Heat Pump** C \rightarrow $H \uparrow$
 takes heat from transfers to

- this is simply a change in view point
- the Carnot cycle can serve as the initial model of the ideal refrigeration cycle.
 - operates as a reversed heat engine cycle - transfers a quantity of heat, Q_L , from a cold source at temperature, T_L

$$Q_L = T_L(s_3 - s_2)$$

$$Q_H = T_H(s_4 - s_1)$$



$$W_{in} = Q_{net} = Q_H - Q_L$$

$$= (T_H - T_L)(s_3 - s_2)$$

The coefficient of performance (COP) is given by

$$COP = \frac{\text{benefit}}{\text{cost}}$$

where the benefit for a refrigeration process is the cooling load given as Q_L . This is the net benefit, i.e. heat is removed from the cold space. For a heat pump, the benefit is the heat added to the hot space, i.e. Q_H .

$$COP_{refrig} = \frac{Q_L}{W_{in}} = \frac{T_L}{T_H - T_L}$$

$$COP_{heat\ pump} = \frac{Q_H}{W_{in}} = \frac{T_H}{T_H - T_L}$$

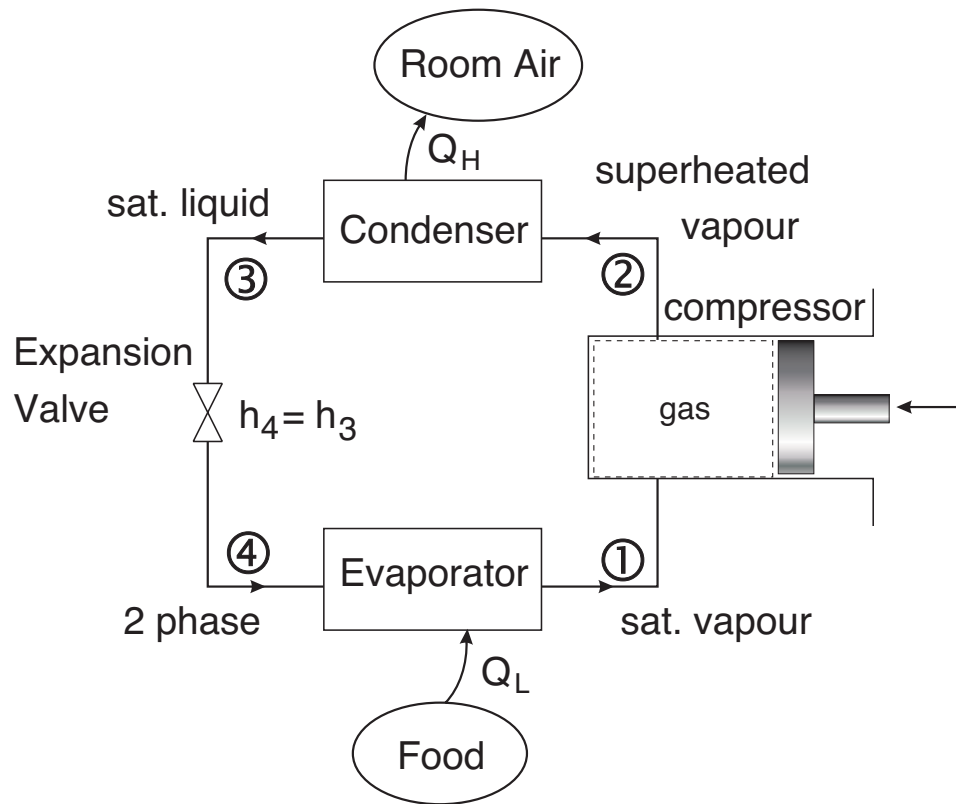
Note:

$$COP_{heat\ pump} = \frac{T_H}{T_H - T_L} = \frac{(T_H - T_L) + T_L}{T_H - T_L} = \frac{T_L}{T_H - T_L} + 1$$

$$= COP_{refrig} + 1$$

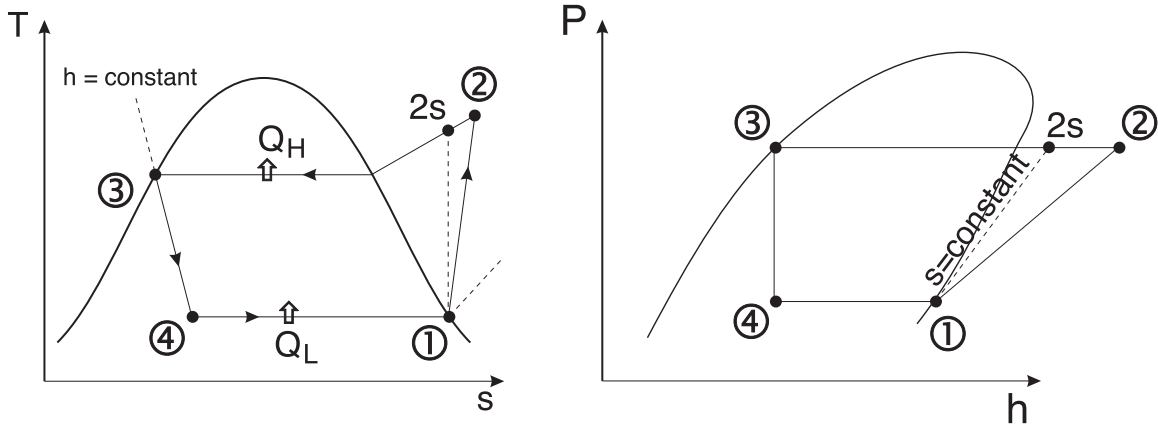
The “1” accounts for the sensible heat addition in going from T_L to T_H .

Vapour Compression Refrigeration Cycle



Assumptions for Ideal VCRC

- irreversibilities within the evaporator, condenser and compressor are ignored
- no frictional pressure drops
- refrigerant flows at constant pressure through the two heat exchangers (evaporator and condenser)
- stray heat losses to the surroundings are ignored
- compression process is isentropic



Refrigeration Process

Process	Description
1-2s:	A reversible, adiabatic (isentropic) compression of the refrigerant. The saturated vapour at state 1 is superheated to state 2. $\Rightarrow w_c = h_{2s} - h_1$
2s-3:	An internally, reversible, constant pressure heat rejection in which the working substance is desuperheated and then condensed to a saturated liquid at 3. During this process, the working substance rejects most of its energy to the condenser cooling water. $\Rightarrow q_H = h_{2s} - h_3$
3-4	An irreversible throttling process in which the temperature and pressure decrease at constant enthalpy. $\Rightarrow h_3 = h_4$
4-1	An internally, reversible, constant pressure heat interaction in which the working fluid is evaporated to a saturated vapour at state point 1. The latent enthalpy necessary for evaporation is supplied by the refrigerated space surrounding the evaporator. The amount of heat transferred to the working fluid in the evaporator is called the refrigeration load. $\Rightarrow q_L = h_1 - h_4$

The thermal efficiency of the cycle can be calculated as

$$\eta = \frac{q_{evap}}{w_{comp}} = \frac{h_1 - h_4}{h_{2s} - h_1}$$

Common Refrigerants

There are several fluorocarbon refrigerants that have been developed for use in VCRC.

R11

R12 CCl_2F_2 dichlorofluoromethane
- used for refrigeration systems at higher temperature levels
- typically, water chillers and air conditioning

R22 $CHClF_2$ has less chlorine, a little better for the environment than R12
- used for lower temperature applications

R134a CFH_2CF_3 tetrafluoroethane - no chlorine
- went into production in 1991
- replacement for R12

R141b $C_2H_3FCl_2$ dichlorofluoroethane

Ammonia NH_3 corrosive and toxic
- used in absorption systems

R744 CO_2 behaves in the supercritical region
- low efficiency

R290 **propane** combustible

How to Choose a Refrigerant

Many factors need to be considered

- ozone depletion potential
- global warming potential
- combustibility
- thermal factors

Ozone Depletion Potential

- chlorinated and brominated refrigerants
- acts as a catalyst to destroy ozone molecules

- reduces the natural shielding effect from incoming ultra violet B radiation

Global Warming Potential

- gases that absorb infrared energy
- gases with a high number of carbon-fluorine bonds
- generally have a long atmospheric lifetime

Combustibility

- all hydro-carbon fuels, such as propane

Thermal Factors

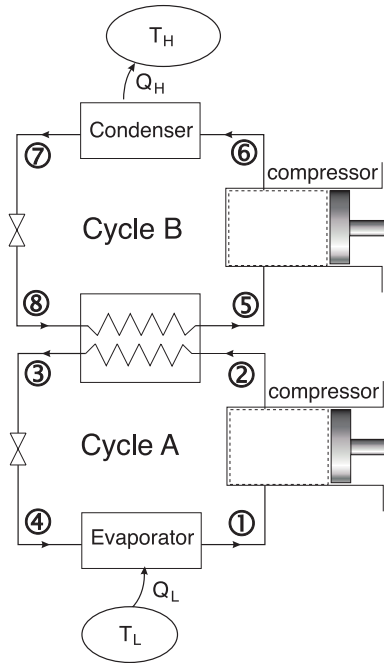
- the heat of vaporization of the refrigerant should be high. The higher h_{fg} , the greater the refrigerating effect per kg of fluid circulated
- the specific heat of the refrigerant should be low. The lower the specific heat, the less heat it will pick up for a given change in temperature during the throttling or in flow through the piping, and consequently the greater the refrigerating effect per kg of refrigerant
- the specific volume of the refrigerant should be low to minimize the work required per kg of refrigerant circulated
- since evaporation and condenser temperatures are fixed by the temperatures of the surroundings - selection is based on operating pressures in the evaporator and the condenser
- selection is based on the suitability of the pressure-temperature relationship of the refrigerant
- other factors include:
 - chemical stability
 - toxicity
 - cost
 - environmental friendliness
 - does not result in very low pressures in the evaporator (air leakage)
 - does not result in very high pressures in the condenser (refrigerant leakage)

Designation	Chemical Formula	Ozone Depletion Potential¹	Global Warming Potential²
<i>Ozone Depleting & Global Warming Chemicals</i>			
CFC-11	CCl_3F	1	3,400
CFC-12	CCl_2F_2	0.89	7,100
CFC-13	$CClF_3$		13,000
CFC-113	$C_2F_3Cl_3$	0.81	4,500
CFC-114	$C_2F_4Cl_2$	0.69	7,000
CFC-115	$C_2F_5Cl_1$	0.32	7,000
Halon-1211	CF_2ClBr	2.2-3.5	
Halon-1301	CF_3Br	8-16	4,900
Halon-2402	$C_2F_4Br_2$	5-6.2	
carbon tetrachloride	CCl_4	1.13	1,300
methyl chloroform	CH_3Ccl_3	0.14	
nitrous oxide	N_2O		270
<i>Ozone Depleting & Global Warming Chemicals - Class 2</i>			
HCFC-22	CHF_2Cl	0.048	1,600
HCFC-123	$C_2HF_3Cl_2$	0.017	90
HCFC-124	C_2HF_4Cl	0.019	440
HCFC-125	C_2HF_5	0.000	3,400
HCFC-141b	$C_2H_3FCl_2$	0.090	580
HCFC-142b	$C_2H_3F_2Cl$	0.054	1800
<i>Global Warming, non-Ozone Depleting Chemicals</i>			
carbon dioxide	CO_2	0	1
methane	CH_4	0	11
HFC-125	CHF_2CF_3	0	90
HFC-134a	CFH_2CF_3	0	1,000
HFC-152a	CH_3CHF_2	0	2,400
perfluorobutane	C_4F_{10}	0	5,500
perfluoropentane	C_5F_{12}	0	5,500
perfluorohexane	C_6F_{14}	0	5,100
perfluorotributylamine	$N(C_4F_9)_3$	0	4,300

1 - relative to R11

2 - relative to CO₂

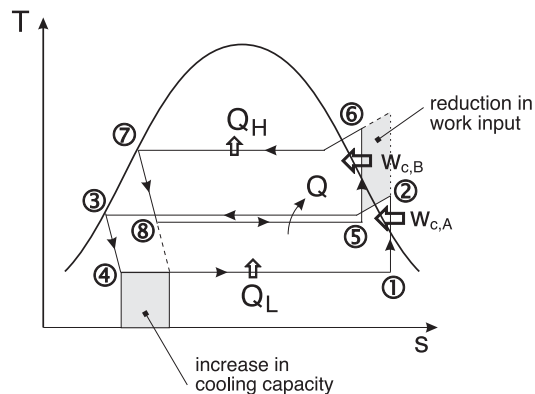
Cascade Refrigeration System



- combined cycle arrangements
- two or more vapour compression refrigeration cycles are combined
- used where a very wide range of temperature between T_L and T_H is required
- the condenser for the low temperature refrigerator is used as the evaporator for the high temperature refrigerator

Advantages

- the refrigerants can be selected to have reasonable evaporator and condenser pressures in the two or more temperature ranges



Absorption Refrigeration System

Differences between an absorption refrigeration system and a VCRC

VCRC

- vapour is compressed between the evaporator and the condenser
- process is driven by work

Absorption RS

- the refrigerant is absorbed by an absorbent material to form a liquid solution
- heat is added to the process to retrieve the refrigerant vapour from the liquid solution
- process is driven by heat

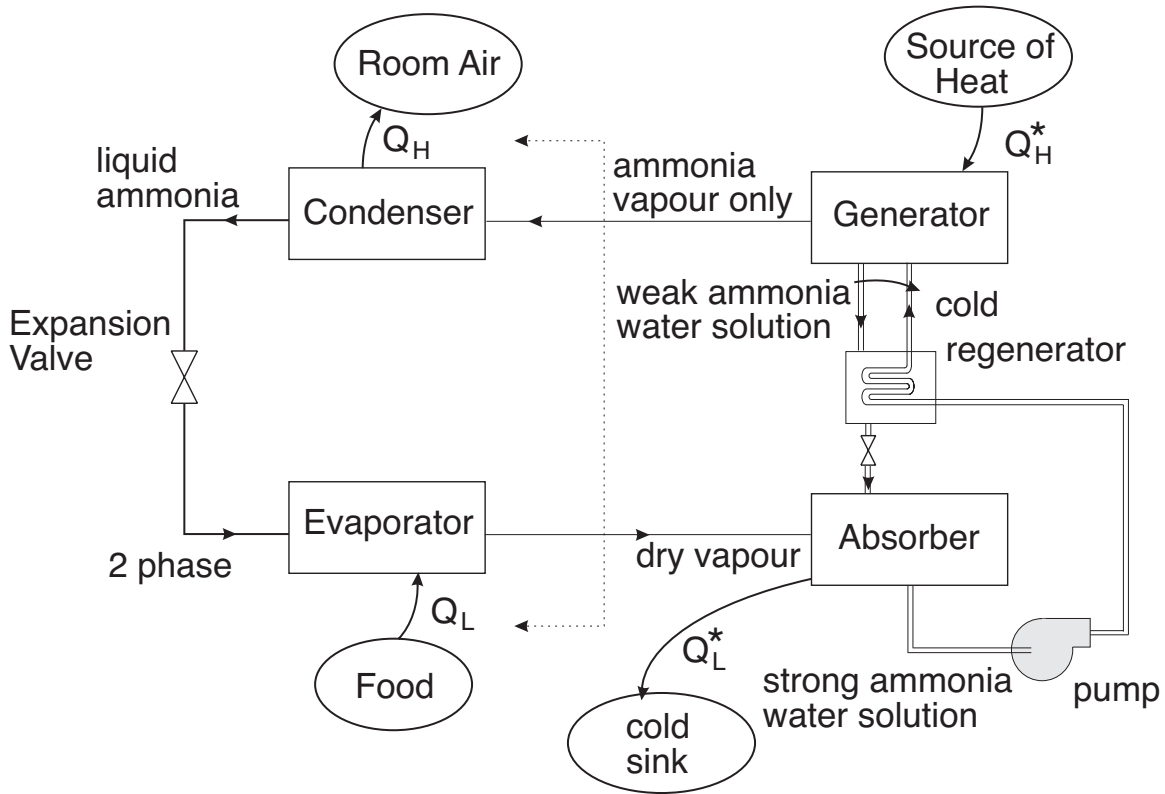
Advantages

- since the working fluid is pumped as a liquid the specific volume is less than that of a gas (as in the VCRC compressor), hence the work input is much less.
- there are considerable savings in power input because a pump is used instead of a compressor.
- this is weighed off against the cost of extra hardware in an absorption system

Common Refrigerant/Absorber Combinations


	<u>Refrigerant</u>	<u>Absorber</u>
1.	ammonia	water
2.	water	lithium bromide lithium chloride

Process



- ammonia circulates through the condenser, expansion valve and evaporator (same as in the VCRC)
- the compressor is replaced by an absorber, pump, generator, regenerator and a valve
- in the absorber, ammonia vapour is absorbed by liquid water
 - the process is exothermic (gives off heat)
 - ammonia vapour is absorbed into the water at low T and P maintained by means of Q_L^*
 - absorption is proportional to $1/T \Rightarrow$ the cooler the better
- the pump raises the solution to the pressure of the generator
- in the generator, ammonia is driven out of the solution by the addition of Q_H^* , (endothermic reaction)
- ammonia vapour is passed back to the condenser
- a regenerator is used to recoup some of the energy from the weak ammonia water solution passed back to the absorber. This energy is transferred to the solution pumped to the generator. This reduces the Q_H^* required to vapourize the solution in the generator. It also reduces the amount of Q_L^* that needs to be removed from the solution in the absorber.

Internal Combustion Engines

	Reading	Problems
	9-3 → 9-7	9-37, 9-41, 9-47, 9-51, 9-56

Definitions

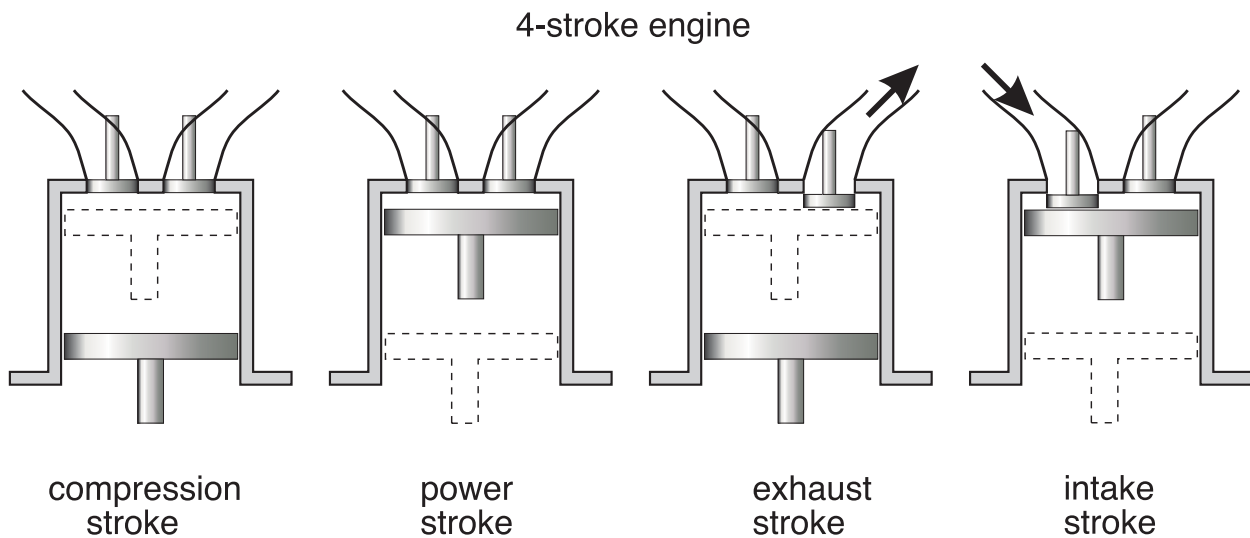
1. spark ignition:

- a mixture of fuel and air is ignited by a spark plug
- applications requiring power to about 225 kW (300 HP)
- relatively light and low in cost

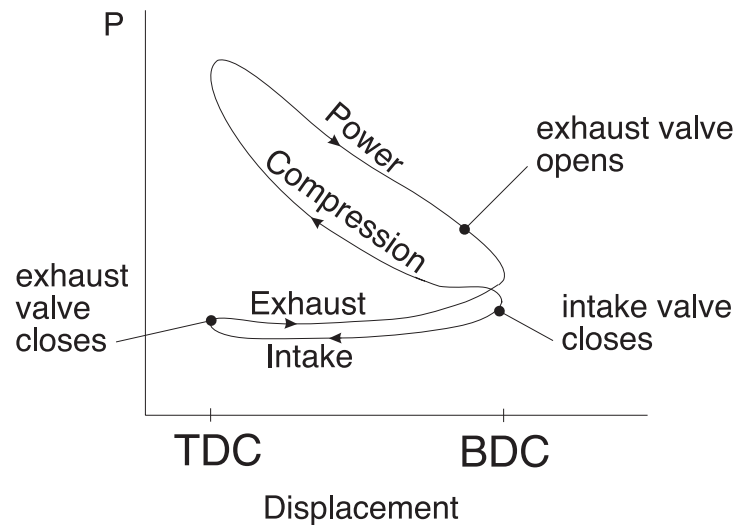
2. compression ignition engine:

- air is compressed to a high enough pressure and temperature that combustion occurs when the fuel is injected
- applications where fuel economy and relatively large amounts of power are required

The Gasoline Engine



- conversion of chemical energy to mechanical energy
- can obtain very high temperatures due to the short duration of the power stroke



Air Standard Cycle

ASSUMPTIONS:

- air is an ideal gas with constant c_p and c_v
- no intake or exhaust processes
- the cycle is completed by heat transfer to the surroundings
- the internal combustion process is replaced by a heat transfer process from a TER
- all internal processes are reversible
- heat addition occurs instantaneously while the piston is at TDC

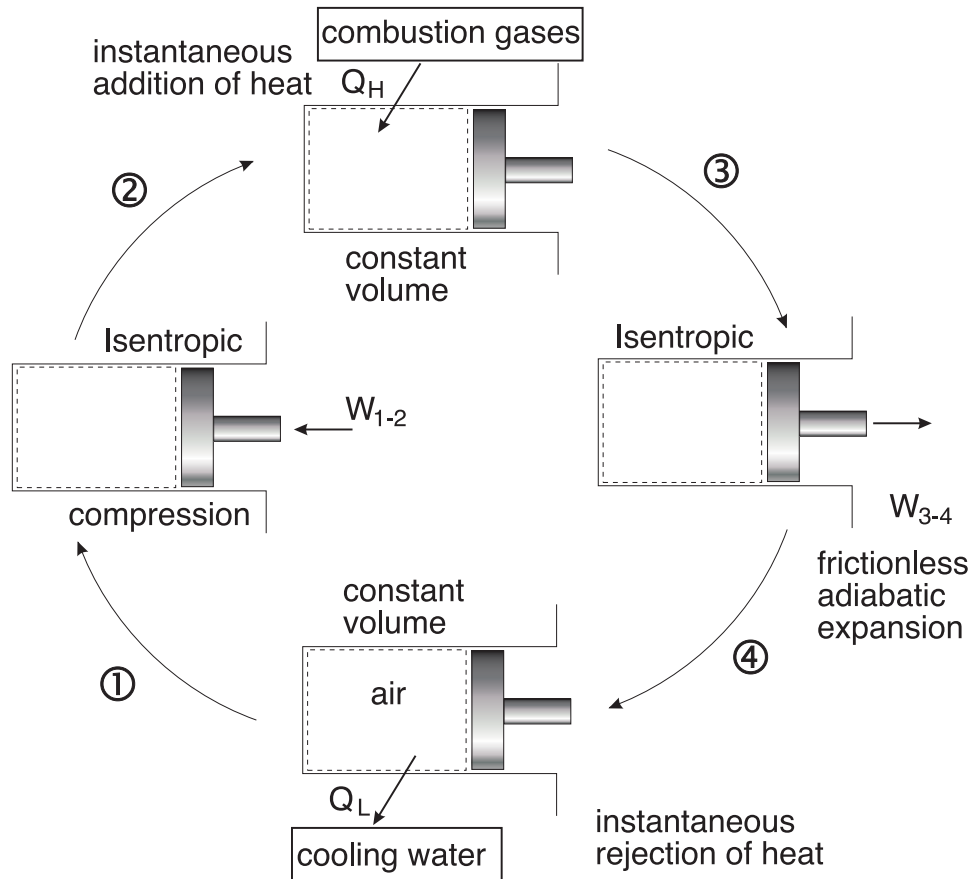
Definitions

Mean Effective Pressure (MEP): The theoretical constant pressure that, if it acted on the piston during the power stroke would produce the same *net* work as actually developed in one complete cycle.

$$MEP = \frac{\text{net work for one cycle}}{\text{displacement volume}} = \frac{W_{net}}{V_{BDC} - V_{TDC}}$$

The mean effective pressure is an index that relates the work output of the engine to its size (displacement volume).

Otto Cycle



- the theoretical model for the gasoline engine
- consists of four internally reversible processes
- heat is transferred to the working fluid at constant volume

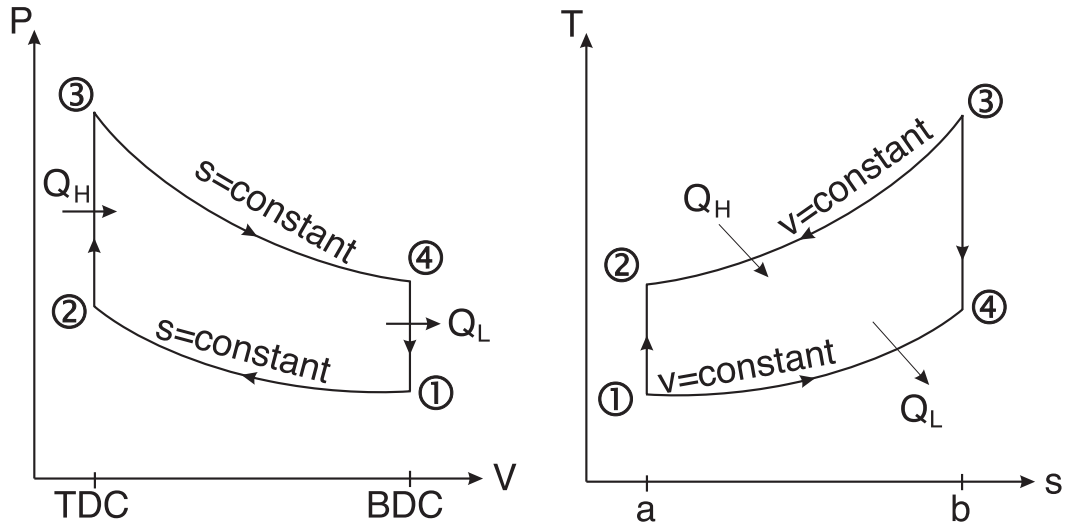
The **Otto cycle** consists of four internally reversible processes in series

1 → **2** isentropic compression or air as the piston moves from BDC to TDC

2 → **3** constant volume heat addition to the fuel/air mixture from an external source while the piston is at TDC (represents the ignition process and the subsequent burning of fuel)

3 → **4** isentropic expansion (power stroke)

4 → **1** constant volume heat rejection at BDC



The Otto cycle efficiency is given as

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{V_2}{V_1}\right)^{k-1} = 1 - \left(\frac{V_1}{V_2}\right)^{1-k}$$

If we let

$$r = \frac{V_1}{V_2} = \frac{V_4}{V_3} = \text{compression ratio}$$

Then

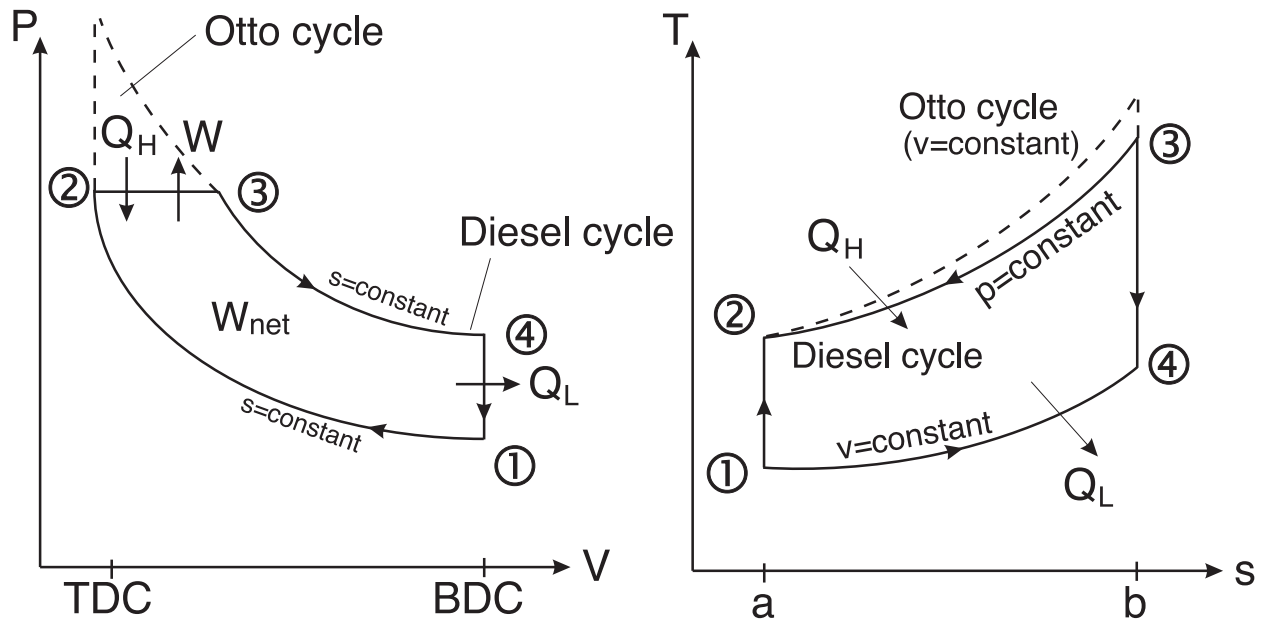
$$\boxed{\eta_{Otto} = 1 - r^{1-k}}$$

Why not go to higher compression ratios?

- there is an increased tendency for the fuel to detonate as the compression ratio increases
- the pressure wave gives rise to engine knock
- can be reduced by adding tetraethyl lead to the fuel
- not good for the environment

Diesel Cycle

- an ideal cycle for the compression ignition engine (diesel engine)
- all steps in the cycle are reversible
- heat is transferred to the working fluid at constant pressure
- heat transfer must be just sufficient to maintain a constant pressure



If we let

$$r = \frac{V_1}{V_2} = \text{compression ratio} = \frac{V_4}{V_2}$$

$$r_v = \frac{V_3}{V_2} = \text{cutoff ratio} \rightarrow \text{injection period}$$

then the diesel cycle efficiency is given as

$$\eta_{Diesel} = 1 - \frac{1}{r^{k-1}} \left(\frac{1}{k} \right) \left(\frac{r_v^k - 1}{r_v - 1} \right)$$

Where we note

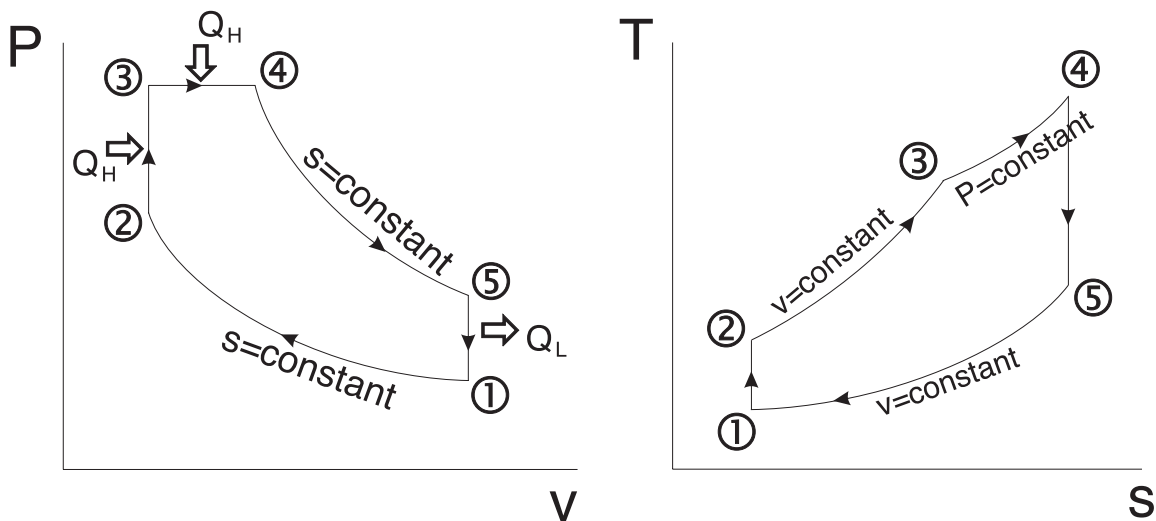
$$\eta_{Diesel} = 1 - \frac{1}{r^{k-1}} \underbrace{\left(\frac{1}{k}\right) \left(\frac{r_v^k - 1}{r_v - 1}\right)}_{=1 \text{ in the Otto Cycle}}$$

Comparison of the Otto and the Diesel Cycle

- $\eta_{Otto} > \eta_{Diesel}$ for the same compression ratio
- but a diesel engine can tolerate a higher ratio since only air is compressed in a diesel cycle and spark knock is not an issue
- direct comparisons are difficult

Dual Cycle (Limited Pressure Cycle)

- this is a better representation of the combustion process in both the gasoline and the diesel engines
- in a compression ignition engine, combustion occurs at TDC while the piston moves down to maintain a constant pressure



Dual Cycle Efficiency

Given

$$r = \frac{V_1}{V_2} = \textit{compression ratio}$$

$$r_v = \frac{V_4}{V_3} = \textit{cutoff ratio}$$

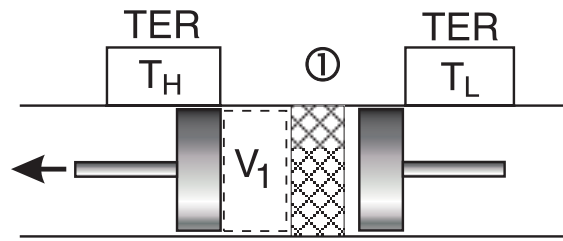
$$r_p = \frac{P_3}{P_2} = \textit{pressure ratio}$$

$$\eta_{Dual} = 1 - \frac{r_p r_v^k - 1}{[(r_p - 1) + k r_p (r_v - 1)] r^{k-1}}$$

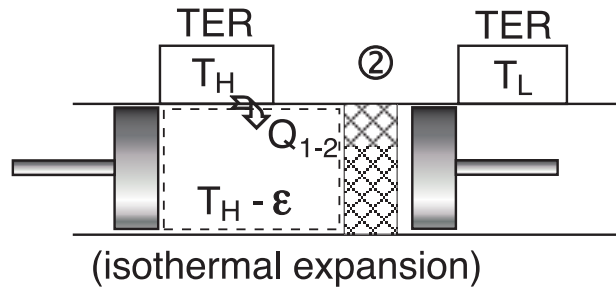
Note: if $r_p = 1$ we get the diesel efficiency.

Stirling Cycle

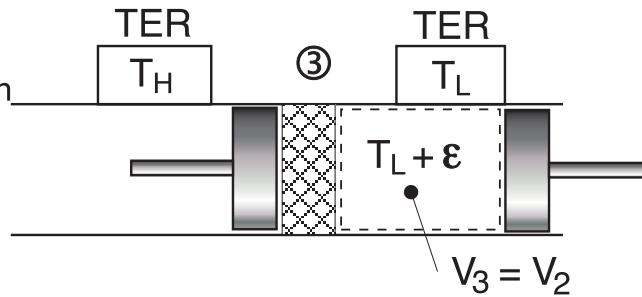
① → ②
 isothermal expansion
 at high temperature
 - heat is added,
 volume expands



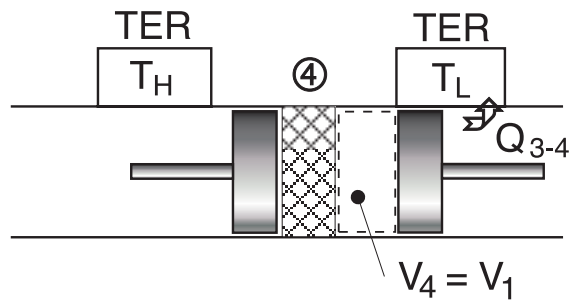
② → ③
 constant volume
 process



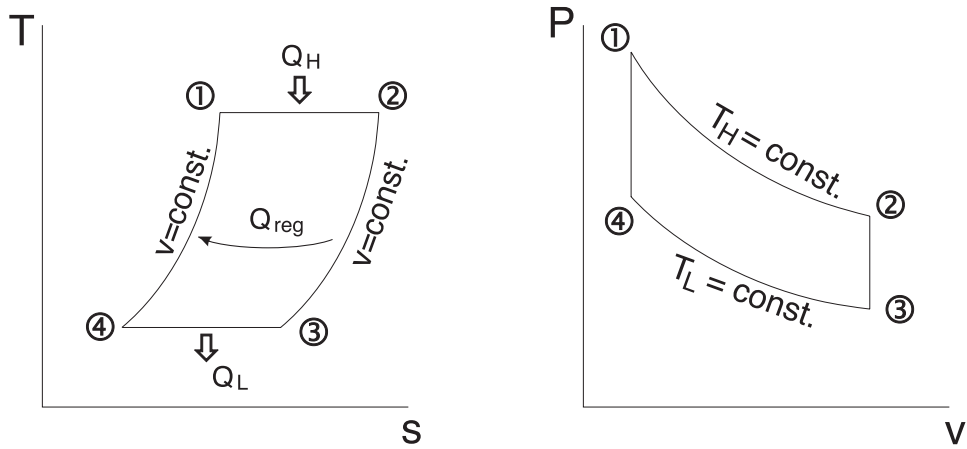
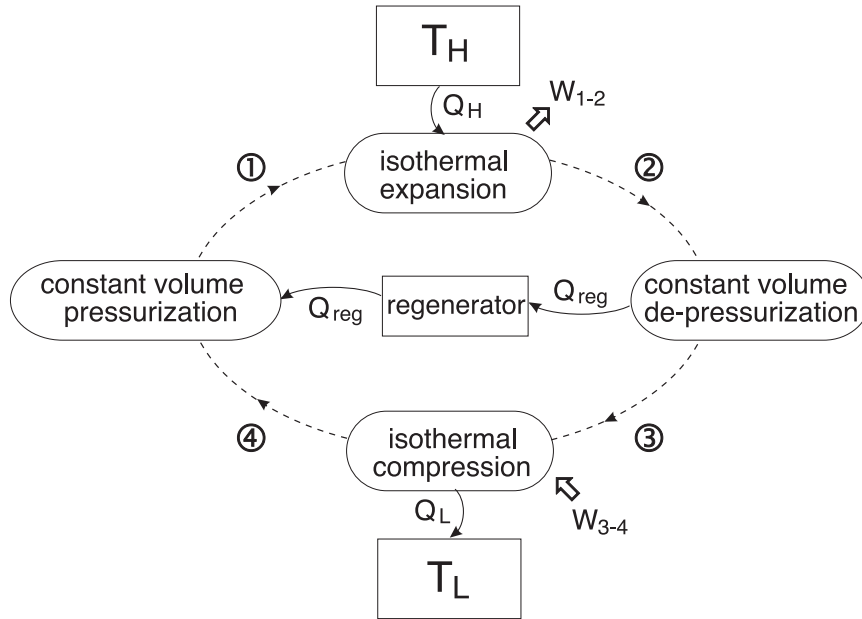
③ → ④
 isothermal compression
 at low temperature



④ → ①
 constant volume
 process



move both pistons
 to the left to get back
 to state 1.
 During this process the
 regenerator cools down
 by giving off energy to
 the gas



- reversible regenerator used as an energy storage device
- possible to recover all heat given up by the working fluid in the constant volume cooling process
- all the heat received by the cycle is at T_H and all heat rejected at T_L
- $\eta_{Stirling} = 1 - T_L/T_H$ (Carnot efficiency)

With perfect regeneration

$$Q_H = T_H(s_2 - s_1)$$

$$Q_L = T_L(s_3 - s_4)$$

$$\eta = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L(s_3 - s_4)}{T_H(s_2 - s_1)} \quad (1)$$

From Gibb's equation

$$Tds = du + Pdv = c_v dT + Pdv$$

$$\text{if } T = \text{constant} \Rightarrow Tds = Pdv \Rightarrow ds = \frac{Pdv}{T} = \frac{Rdv}{v}$$

Integrating gives

$$s_3 - s_4 = R \ln \left(\frac{v_3}{v_4} \right) = R \ln \left(\frac{v_2}{v_1} \right) = s_2 - s_1$$

Therefore $s_3 - s_4 = s_2 - s_1$, and Eq. 1 gives

$$\eta = 1 - \frac{T_L}{T_H} \Rightarrow \text{Carnot efficiency}$$

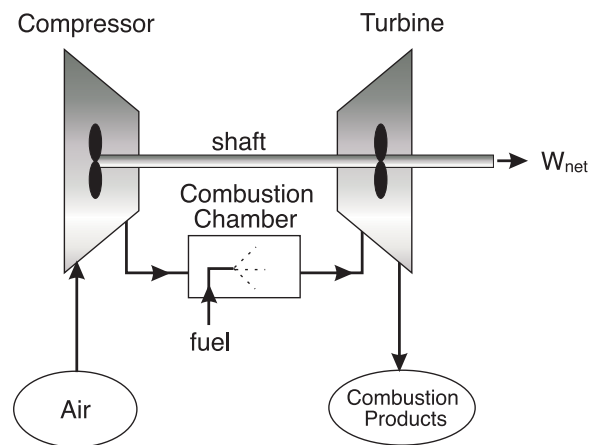
Brayton Cycle



Reading
9-8 → 9-10

Problems
9-78, 9-84, 9-108

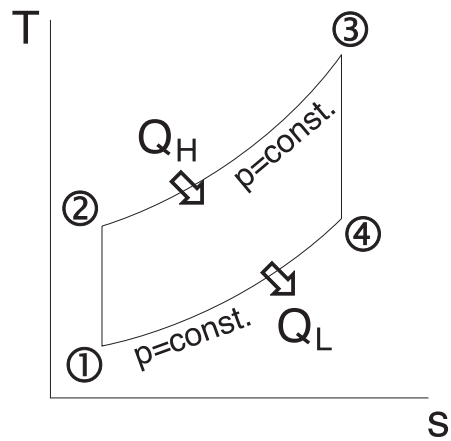
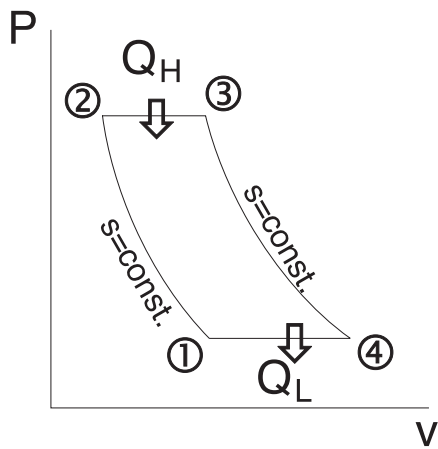
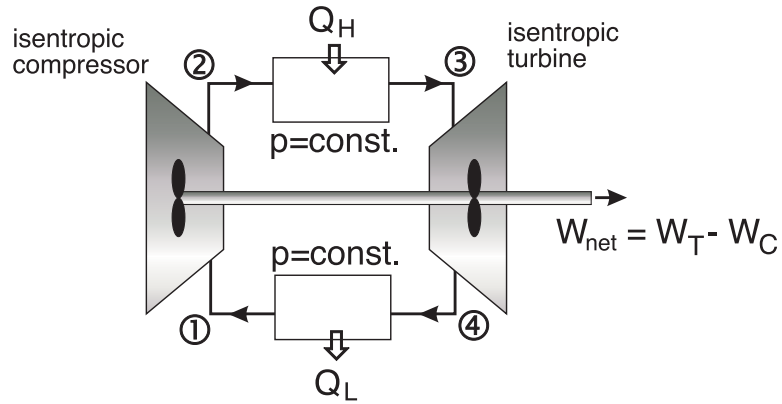
Open Cycle Gas Turbine Engines



- after compression, air enters a combustion chamber into which fuel is injected
- the resulting products of combustion expand and drive the turbine
- combustion products are discharged to the atmosphere
- compressor power requirements vary from 40-80% of the power output of the turbine (remainder is net power output), i.e. back work ratio = 0.4 → 0.8
- high power requirement is typical when gas is compressed because of the large specific volume of gases in comparison to that of liquids

Idealized Air Standard Brayton Cycle

- closed loop
- constant pressure heat addition and rejection
- ideal gas with constant specific heats



Brayton Cycle Efficiency

The Brayton cycle efficiency can be written as

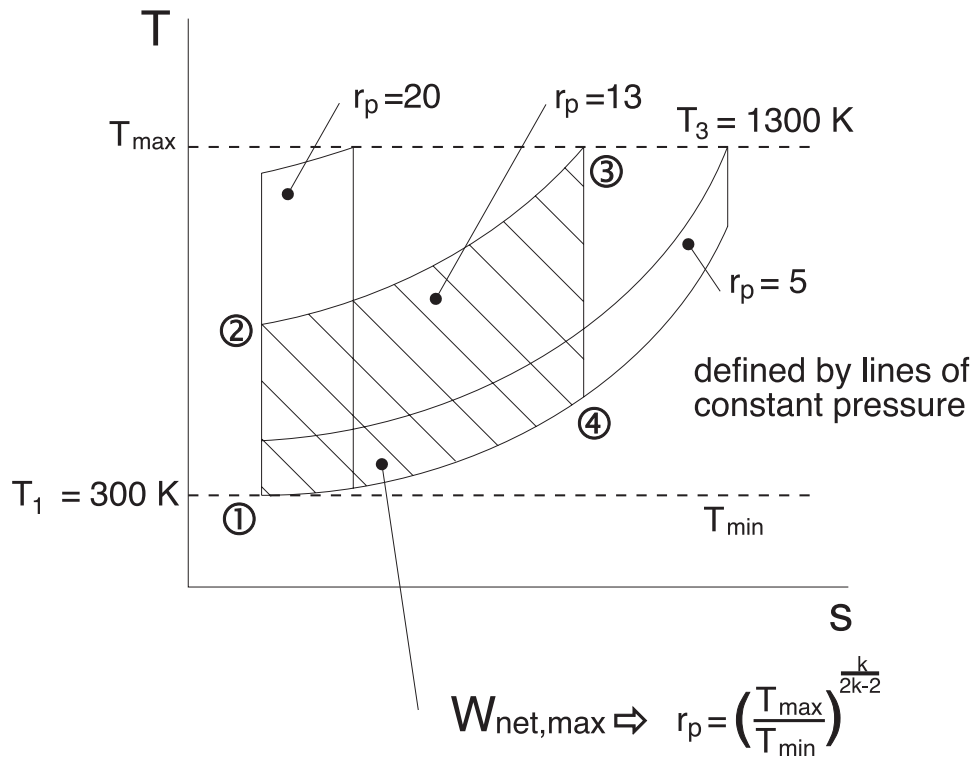
$$\eta = 1 - (r_p)^{(1-k)/k}$$

where we define the pressure ratio as:

$$r_p = \frac{P_2}{P_1} = \frac{P_3}{P_4}$$

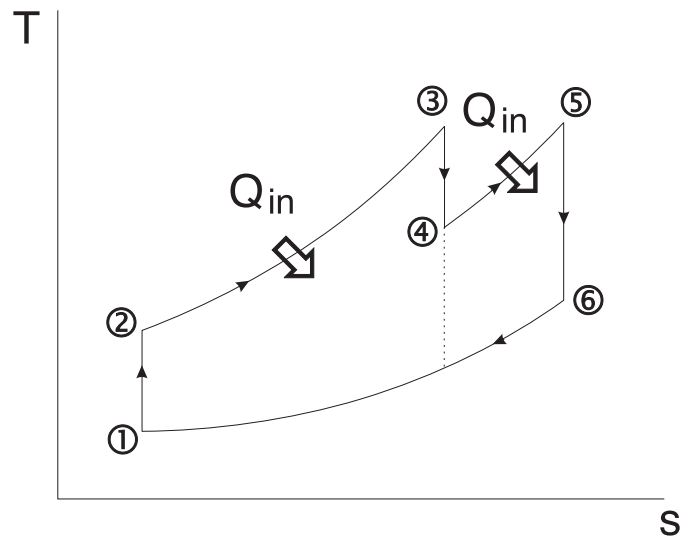
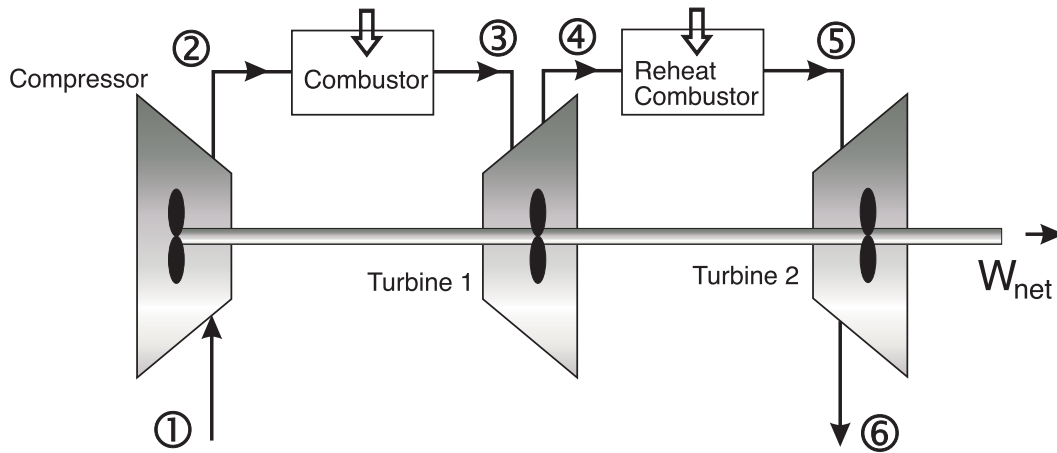
Maximum Pressure Ratio

Given that the maximum and minimum temperature can be prescribed for the Brayton cycle, a change in the pressure ratio can result in a change in the work output from the cycle.



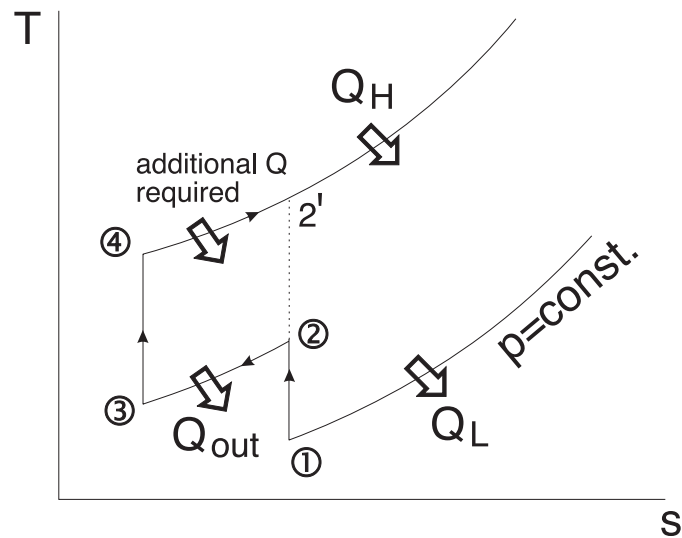
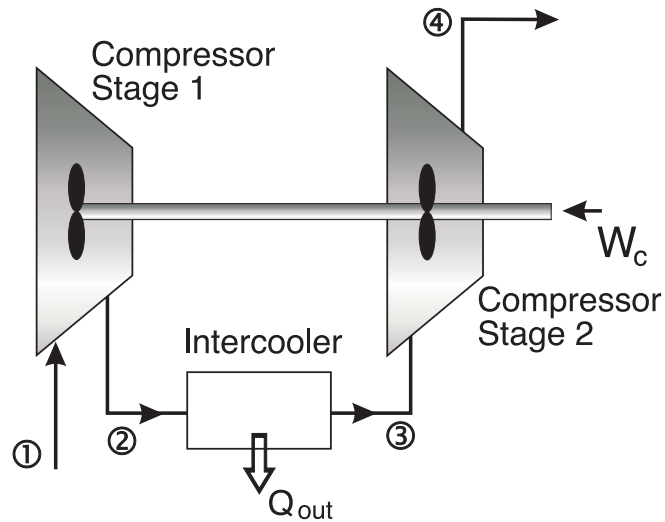
The **maximum temperature** in the cycle (T_3) is limited by metallurgical conditions because the turbine blades cannot sustain temperatures above 1300 K. Higher temperatures (up to 1600 K can be obtained with ceramic turbine blades). The **minimum temperature** is set by the air temperature at the inlet to the engine.

Brayton Cycle with Reheat



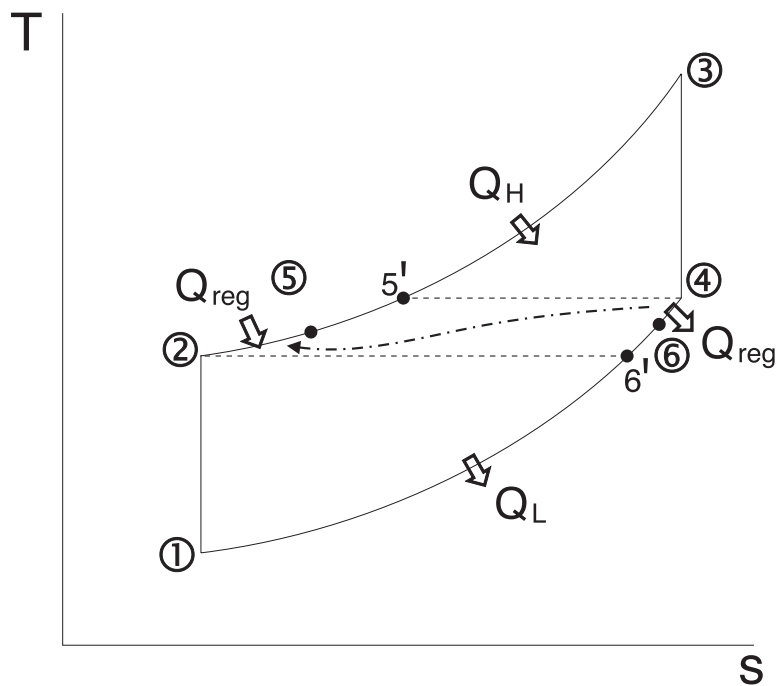
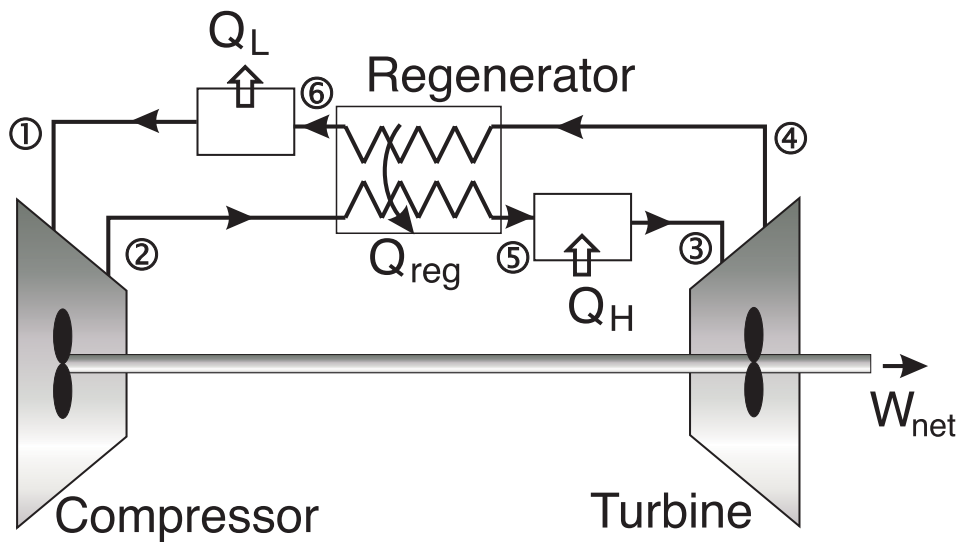
- T_3 is limited due to metallurgical constraints
- excess air is extracted and fed into a second stage combustor and turbine
- turbine outlet temperature is increased with reheat ($T_6 > T_4'$), therefore potential for regeneration is enhanced
- when reheat and regeneration are used together the thermal efficiency can increase significantly

Compression with Intercooling



- the work required to compress in a steady flow device can be reduced by compressing in stages
- cooling the gas reduces the specific volume and in turn the work required for compression
- by itself compression with intercooling does not provide a significant increase in the efficiency of a gas turbine because the temperature at the combustor inlet would require additional heat transfer to achieve the desired turbine inlet temperature
- but the lower temperature at the compressor exit enhances the potential for regeneration i.e. a larger ΔT across the heat exchanger

Brayton Cycle with Regeneration



- a regenerator (heat exchanger) is used to reduce the fuel consumption to provide the required \dot{Q}_H
- the efficiency with a regenerator can be determined as:

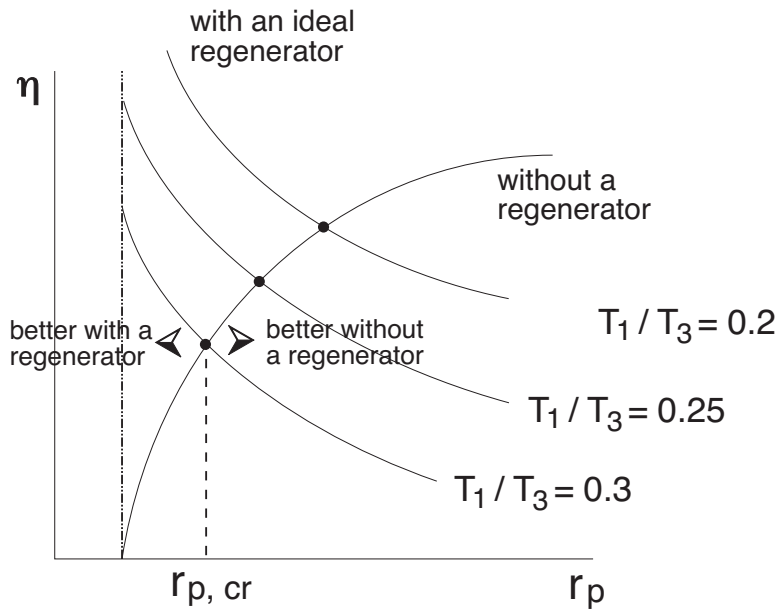
$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_H} = 1 - \frac{\dot{Q}_L}{\dot{Q}_H}$$

$$\begin{aligned}
 &= 1 - \frac{c_p(T_6 - T_1)}{c_p(T_3 - T_5)} \Rightarrow \text{(for a real regenerator)} \\
 &= 1 - \frac{c_p(T'_6 - T_1)}{c_p(T_3 - T'_5)} \Rightarrow \text{(for an ideal regenerator)} \\
 &= 1 - \frac{c_p(T_2 - T_1)}{c_p(T_3 - T_4)}
 \end{aligned}$$

and

$$\eta = 1 - \left(\frac{T_{min}}{T_{max}} \right) (r_p)^{(k-1)/k}$$

- for a given T_{min}/T_{max} , the use of a regenerator above a certain r_p will result in a reduction of η



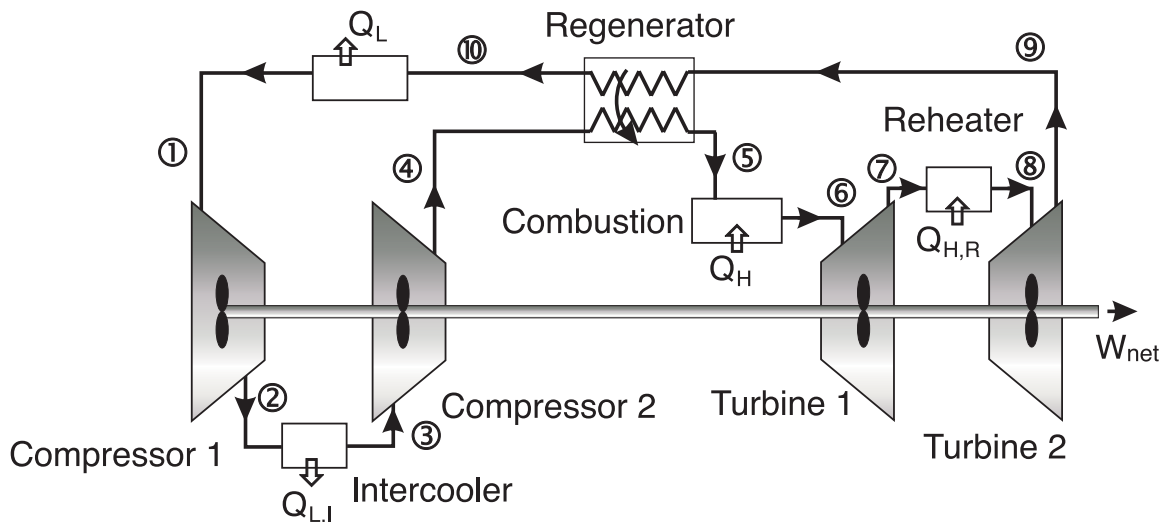
Regenerator Effectiveness

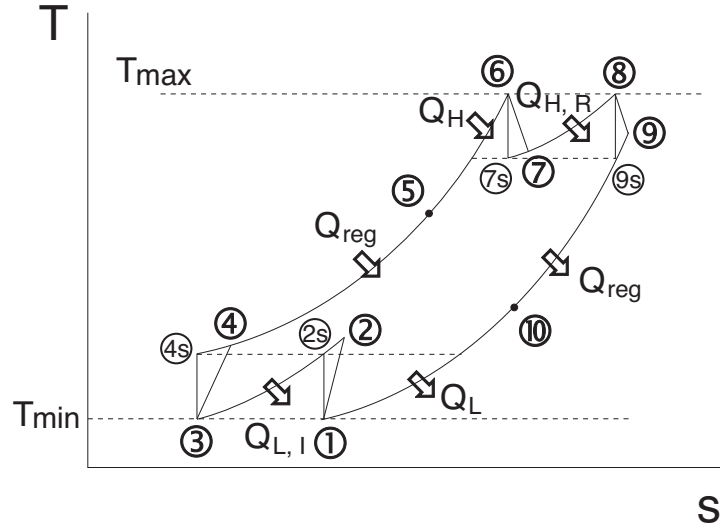
$$\epsilon = \frac{\dot{Q}_{reg,actual}}{\dot{Q}_{reg,ideal}} = \frac{h_5 - h_2}{h'_5 - h_2} = \frac{h_5 - h_2}{h_4 - h_2} = \frac{T_5 - T_2}{T_4 - T_2}$$

Typical values of effectiveness are ≤ 0.7

Repeated intercooling, reheating and regeneration will provide a system that approximates the Ericsson Cycle which has Carnot efficiency $\left(\eta = 1 - \frac{T_L}{T_H}\right)$.

Brayton Cycle With Intercooling, Reheating and Regeneration





Compressor and Turbine Efficiencies

Isentropic Efficiencies

$$(1) \quad \eta_{comp} = \frac{h_{2,s} - h_1}{h_2 - h_1} = \frac{c_p(T_{2,s} - T_1)}{c_p(T_2 - T_1)}$$

$$(2) \quad \eta_{turb} = \frac{h_3 - h_4}{h_3 - h_{4,s}} = \frac{c_p(T_3 - T_4)}{c_p(T_3 - T_{4,s})}$$

$$(3) \quad \eta_{cycle} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{c_p(T_4 - T_1)}{c_p(T_3 - T_2)}$$

Given the turbine and compressor efficiencies and the maximum (T_3) and the minimum (T_1) temperatures in the process, find the cycle efficiency (η_{cycle}).

- (4) Calculate T_{2s} from the isentropic relationship,


$$\frac{T_{2,s}}{T_1} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k}$$

Get T_2 from (1).

- (5) Do the same for T_4 using (2) and the isentropic relationship.

- (6) substitute T_2 and T_4 in (3) to find the cycle efficiency.

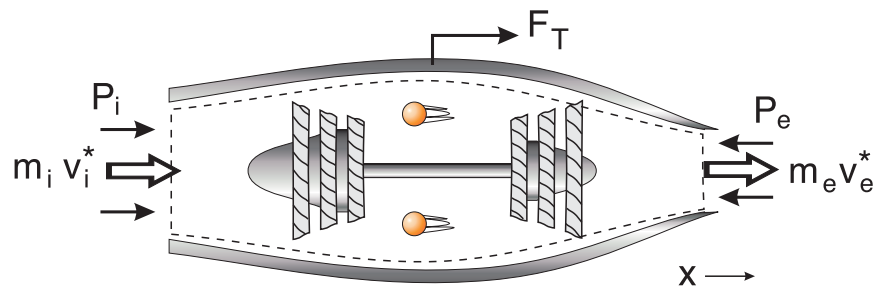
Jet Propulsion

	Reading	Problems
	9-11	9-117, 9-121

Gas Turbines for Aircraft Propulsion

- gas turbines are well suited to aircraft propulsion because of their favorable power-to-weight ratio
- the exhaust pressure of the turbine will be greater than that of the surroundings
- gases are expanded in the turbine to a pressure where the turbine work is just equal to the compressor work plus some auxiliary power for pumps and generators i.e. the net work output is zero
- since the gases leave at a high velocity, the change in momentum that the gas undergoes provides a thrust to the aircraft
- typically operate at higher pressure ratios, often in the range of 10 to 25

Conservation of Momentum



where v_i^* is the velocity of the aircraft

$$\frac{d(\text{Mom})_{x,cv}}{dt} = (\dot{\text{Mom}})_{x,in} - (\dot{\text{Mom}})_{x,out} + \sum F_x$$

for steady flow $\Rightarrow \frac{d}{dt} = 0$ and

$$\dot{m}_i v_i^* - \dot{m}_e v_e^* + F_T + P_i A_i - P_e A_e = 0$$

Since the air-fuel mass ratio is high

$$\dot{m}_{fuel} \ll \dot{m}_i \quad \Rightarrow \quad \dot{m}_i \approx \dot{m}_e$$

and

$$P_e \approx P_i \approx P_{atm}$$

Therefore

$$\begin{aligned} F_T &= \dot{m}_e v_e^* - \dot{m}_i v_i^* - \underbrace{P_{atm}(A_i - A_e)}_{negligible} \\ &= \dot{m}_i (v_e^* - v_i^*) \end{aligned}$$

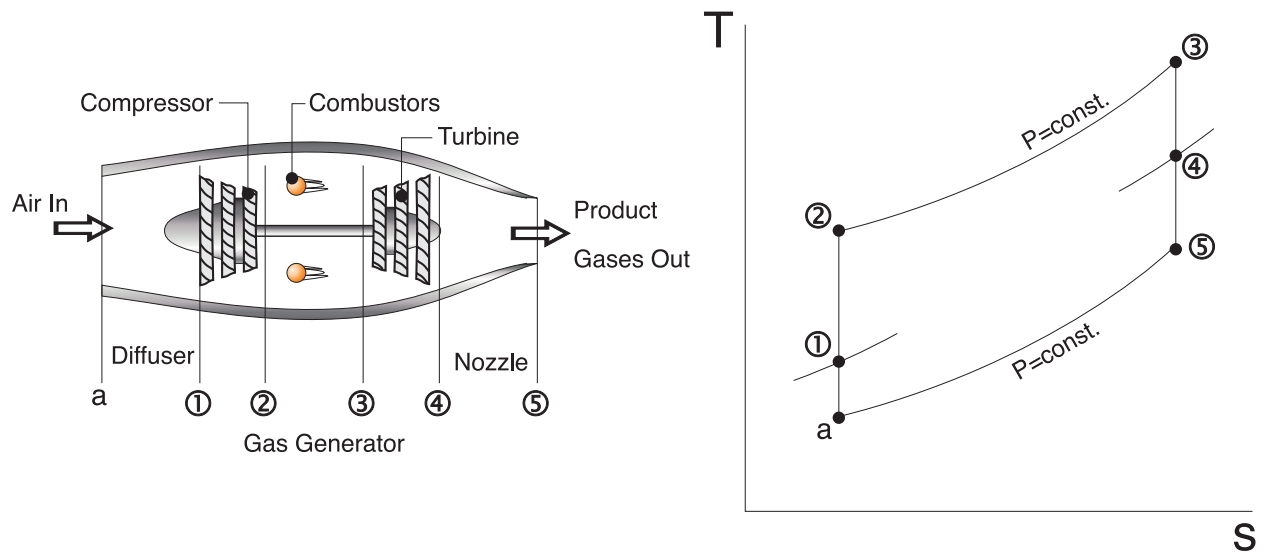
$$\text{Specific Impulse: } I = \frac{F_T}{\dot{m}_i} = v_e^* - v_i^* = \frac{\text{thrust}}{\text{mass}}$$

$$\text{Propulsive Power: } \dot{W}_T = F_T v_i^* \approx \dot{m}_i (v_e^* - v_i^*) v_i^*$$

$$\text{Propulsive Efficiency: } \eta = \frac{\dot{W}_T}{\dot{Q}_{in}}$$

Since the net work output is zero, we must define the propulsive efficiency as propulsive power over the heat flow rate in the combustion process. This then becomes a measure of how efficiently the energy released during the combustion process is converted to propulsive energy.

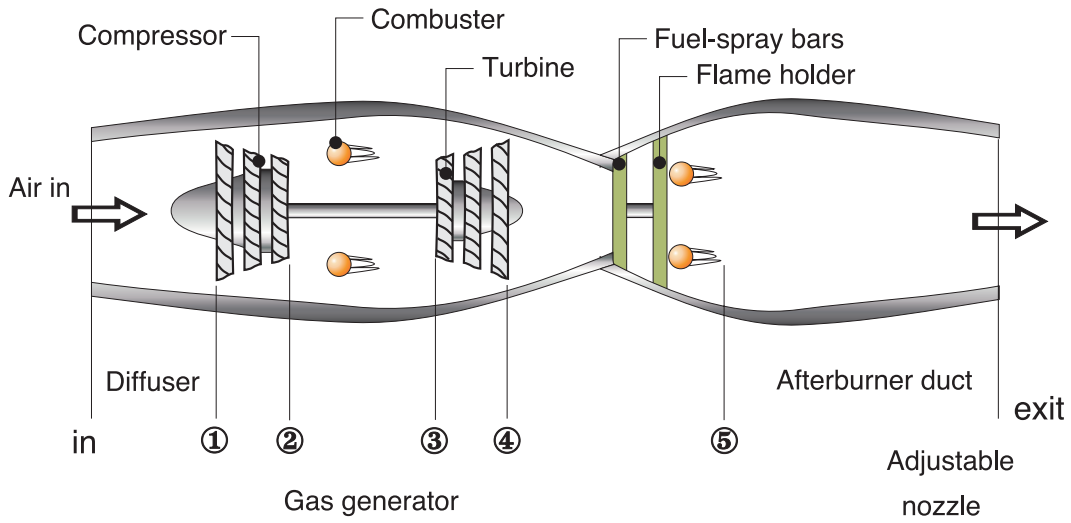
Turbojet Engine



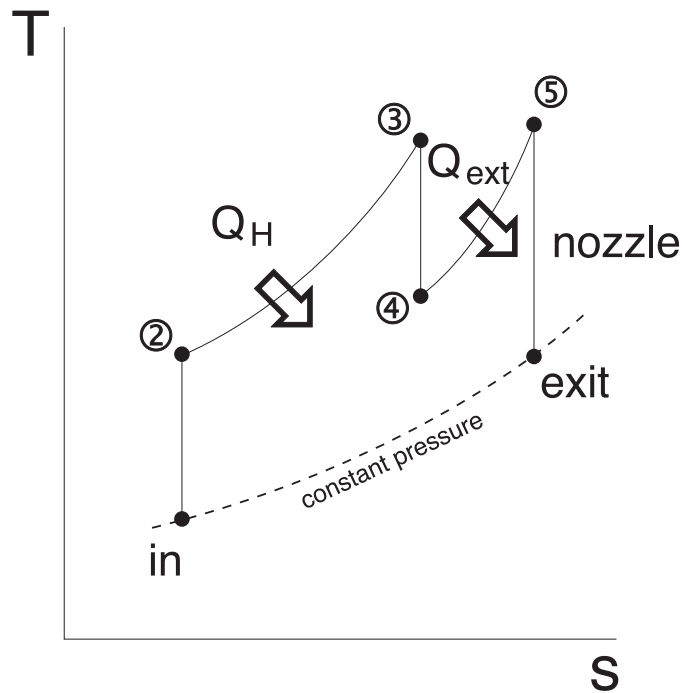
Sections

- **a-1: diffuser**
 - decelerates the incoming flow relative to the engine
 - a pressure rise known as a ram effect occurs, $v^* (\downarrow)$, $P (\uparrow)$
- **1-4: gas generator**
 - compressor, combustor and turbine
 - * 1-2: isentropic compression
 - * 2-3: constant pressure heat addition
 - * 3-4: isentropic expansion through the turbine during which work is developed
 - turbine power just enough to drive the compressor
 - air and fuel are mixed and burned in the combustion chamber at constant pressure
 - $P_T \gg P_{atm}$
- **4-5: nozzle**
 - isentropic expansion through the nozzle, air accelerates and the pressure decreases
 - gases leave the turbine significantly higher in pressure than atmospheric pressure
 - gases are expanded to produce a high velocity, $v_e^* \gg v_i^*$ results in a thrust
 - $v_1^* \ll v_a^*$ v_1^* is negligible
 - $v_4^* \ll v_5^*$ v_4^* is negligible

Afterburner



- similar to a reheat device
- produces a higher temperature at the nozzle inlet, $T_5 > T_4$
- results in an increase in velocity



By performing a 1st law energy over the nozzle we can obtain an expression for the exit velocity in terms of the entrance temperature to the nozzle.

$$\frac{dE^0}{dt} = \dot{Q}^0 + \dot{W}^0 + \left\{ \dot{m} \left[h_4 + \underbrace{\frac{(v_4^*)^2}{2}}_{\rightarrow 0} \right] \right\} - \left\{ \dot{m} \left[h_e + \frac{(v_e^*)^2}{2} \right] \right\}$$

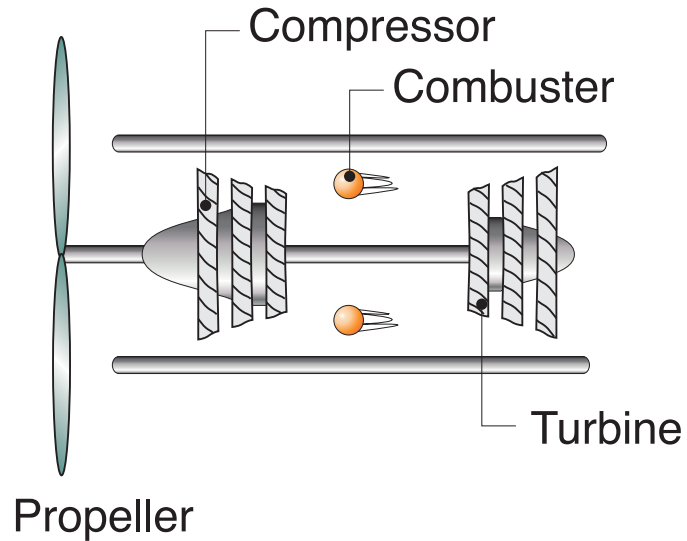
If we assume that the air velocity leaving the turbine is relatively small, the kinetic energy term at 4 can be assumed to go to zero and we get

$$\begin{aligned} v_e^* &= \sqrt{2(h_4 - h_e)} \\ &= \sqrt{2c_p(T_4 - T_e)} \end{aligned}$$

- exit velocity proportional to $v_e^* \propto \sqrt{2c_p(T_4 - T_e)}$
- afterburner is used to increase T_4 to T_5
- similar to a reheat device
- produces a higher temperature at the nozzle inlet

Other Types of Engines

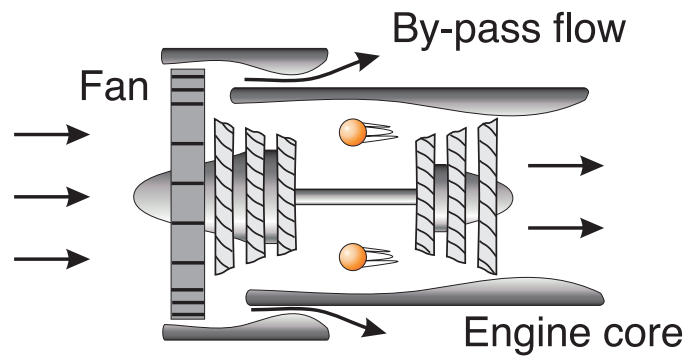
1. Turbo-Prop Engine



- gas turbine drives the compressor and the propeller
- most of the thrust is from the propeller
- works by accelerating large volumes of air to moderate velocities
- propellers are best suited for low speed (< 300 mph) flight
- new turbo-props are suitable for velocities up to 500 mph
- by-pass ratio of 100:1 or more
- by-pass ratio defined as:

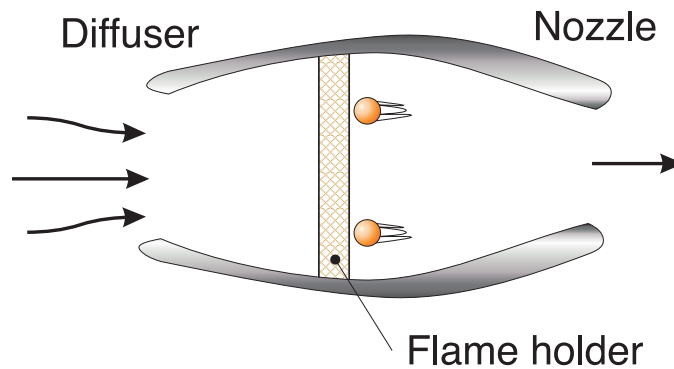
$$\text{bypass ratio} = \frac{\text{mass flow bypassing the combustion chamber}}{\text{mass flow through the combustion chamber}}$$

2. Turbo-Fan Engine (Ducted Turbo-Prop Engine)



- best choice for fuel economy and speed
- high speed exhaust gases are mixed with the lower speed air in the by-pass resulting in a considerable noise reduction
- by-pass ratio can be adjusted
- by-pass provides thrust for takeoff
- the core provides thrust for cruising
- typically used for speeds up to 600 mph
- increasing the by-pass ratio results in increased thrust
- typical by-pass ratios are 5-6

3. Ramjet




- no moving parts
- compression is achieved by decelerating the high-speed incoming air in the diffuser
- aircraft must already be in flight at a high speed
- used in aircraft flying above Mach 1

4. Pulse Jet Engine

- similar to a ram jet but lets in a slug of air at a time and then closes a damper during the combustion stage
- uses a shutter-type valve for damper control
- can be used effectively at low velocities
- used in German V1 missile
- the combustion firing rate was approximately 40 cycles/sec with a maximum flight velocity of 600 mph

Non-Reacting Gas Mixtures

	Reading	Problems
	13-1 → 13-3	13-52, 13-60
	14-1 → 14-7	14-32, 14-35, 14-68, 14-71, 14-75 14-79, 14-103, 14-112

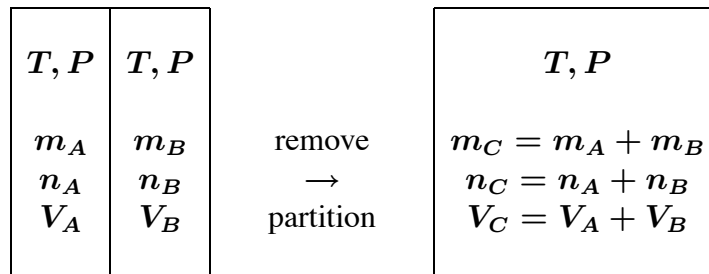
Introduction

- homogeneous gas mixtures are frequently treated as a single compound rather than many individual constituents
- the individual properties of inert gases tend to be submerged, such that the gas behaves as a single pure substance
- eg. - air consists of oxygen, nitrogen, argon and water vapour. But dry air can be treated as a simple gas with a molar mass of **28.97 kg/kmole**
- equations can be derived to express the properties of mixtures in terms of the properties of their individual constituents
- it is assumed that each constituent is unaffected by the other constituents in the mixture

P-V-T Relationships for Ideal Gas Mixtures

Amagat Model (law of additive volumes)

- the volume of a mixture is the sum of the volumes that each constituent gas would occupy if each were at the pressure, P and temperature, T , of the mixture



- the volume that n_i moles of a component i would occupy at P and T is called the partial volume, V_i

$$V_i = \frac{n_i \mathcal{R} T}{P}$$

The volume of the gas mixture is equal to the sum of the volumes each gas would occupy if it existed at the mixture temperature and pressure.

$$V = \sum_{i=1}^j V_i$$

Dalton Model (law of additive pressures)

- the pressure of a mixture of gases is the sum of the pressures of its components when each alone occupies the volume of the mixture, V , at the temperature, T , of the mixture

$$\begin{array}{|c|} \hline V, T \\ \hline m_A, n_A, P_A \\ \hline \end{array} + \begin{array}{|c|} \hline V, T \\ \hline m_B, n_B, P_B \\ \hline \end{array} = \begin{array}{|c|} \hline V, T \\ \hline m_C = m_A + m_B \\ n_C = n_A + n_B \\ P_C = P_A + P_B \\ \hline \end{array}$$

- for a mixture of ideal gases the pressure is the sum of the partial pressures of the individual components

The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at T and V .

By combining the results of the Amagat and Dalton models i.e. (1) and (2), we obtain for ideal gas mixtures

$$\frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n}$$

Therefore, Amagat's law and Dalton's law are equivalent to each other if the gases and the mixture are ideal gases.

Mixture Properties

Extensive properties such as U , H , c_p , c_v and S can be found by adding the contribution of each component at the condition at which the component exists in the mixture.

$$\begin{aligned}U &= \sum U_i = \sum m_i u_i = m \sum X_i u_i = m u \\ &= \sum n_i \bar{u}_i = n \sum Y_i \bar{u}_i = n \bar{u}\end{aligned}$$

where \bar{u} is the specific internal energy of the mixture per mole of the mixture.

$u = \sum X_i u_i$
$h = \sum X_i h_i$
$c_v = \sum X_i c_{v_i}$
$c_p = \sum X_i c_{p_i}$
$s = \sum X_i s_i$

Changes in internal energy and enthalpy of mixtures

$$u_2 - u_1 = \sum X_i (u_2 - u_1)_i = \int_{T_1}^{T_2} c_v dT = c_v (T_2 - T_1)$$

$$h_2 - h_1 = \sum X_i (h_2 - h_1)_i = \int_{T_1}^{T_2} c_p dT = c_p (T_2 - T_1)$$

$$s_2 - s_1 = \sum X_i (s_2 - s_1)_i = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

These relationships can also be expressed on a per mole basis.

Entropy Change Due to Mixing of Ideal Gases

- when ideal gases are mixed, a change in entropy occurs as a result of the increase in disorder in the systems
- if the initial temperature of all constituents are the same and the mixing process is adiabatic

- temperature does not change
- but entropy does

$$\begin{aligned}\Delta S &= -\left(m_A R_A \ln \frac{P_A}{P} + m_B R_B \ln \frac{P_B}{P} + \dots\right) \\ &= -\sum_{i=1}^j m_i R_i \ln \frac{P_i}{P} \\ &= -\mathcal{R} \sum_{i=1}^j n_i \ln Y_i\end{aligned}$$

Psychrometrics

- studies involving mixtures of dry air and water vapour
- used in the design of air-conditioning systems, cooling towers and most processes involving the control of vapour content in air
- for $T \leq 50^\circ C$ ($P_{sat} \leq 13 \text{ kPa}$) $\Rightarrow h \approx h(T)$
 - water vapour can be treated as an ideal gas

Definitions

Moist Air

- a mixture of dry air and water vapour where dry air is treated as if it were a pure component
- the overall mixture is given as $\Rightarrow P = \frac{mRT}{V}$

Total Pressure

$$P = P_a + P_w$$

$$P_a = \frac{m_a R_a T}{V}$$

$$P_w = \frac{m_w R_w T}{V}$$

where P_a is the partial pressure of air and P_w is the partial pressure of water vapour. Typically $m_w \ll m_a$.

Relative Humidity - ϕ

$$\phi = \frac{P_w(T)}{P_{sat}(T)} = \frac{\text{vapour pressure at the prevailing T}}{\text{saturation pressure at the prevailing T}}$$

If $P_w = P_{sat}(T)$ the mixture is said to be saturated.

Specific Humidity (Humidity ratio) - ω

$$\omega = \frac{m_w}{m_a} = \frac{\text{mass of water vapour}}{\text{mass of air}}$$

$$\begin{aligned}
&= \frac{\tilde{M}_w n_w}{\tilde{M}_a n_a} = \frac{\tilde{M}_w (P_w V / \mathcal{R}T)}{\tilde{M}_a (P_a V / \mathcal{R}T)} \\
&= \left(\frac{\tilde{M}_w}{\tilde{M}_a} \right) \left(\frac{P_w}{P_a} \right) \\
&= 0.622 \left(\frac{P_w}{P_a} \right)
\end{aligned}$$

In addition ω can be written as

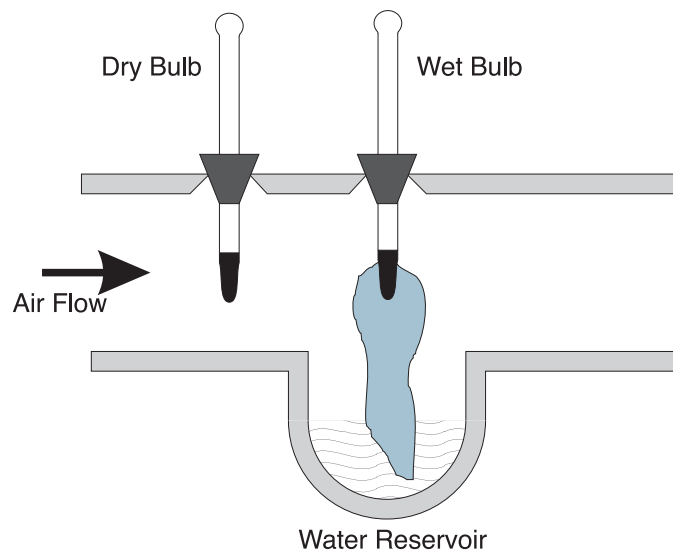
$$\omega = 0.622 \left(\frac{P_w}{P_a} \right) = 0.622 \left(\frac{P_w}{P - P_w} \right) = 0.622 \left(\frac{\phi P_{sat}}{P - \phi P_{sat}} \right)$$

which can be rearranged in terms of relative humidity

$$\phi = \frac{P\omega}{P_{sat} \left(\omega + \frac{\tilde{M}_w}{\tilde{M}_a} \right)} = \frac{P\omega}{P_{sat}(\omega + 0.622)}$$

Dry Bulb Temperature - the temperature measured by a thermometer placed in a mixture of air and water vapour

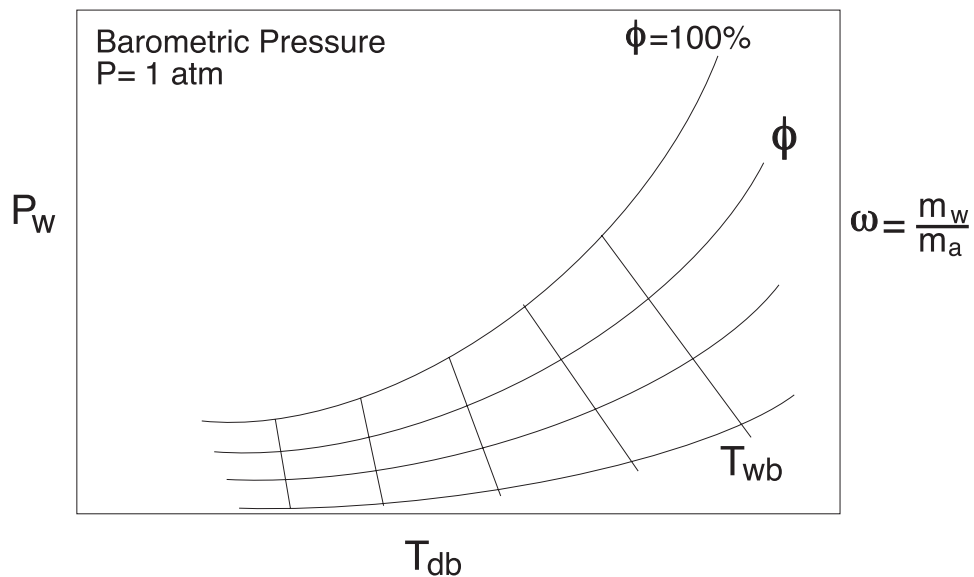
Wet Bulb Temperature



- thermometer surrounded by a saturated wick
- if air/water vapour mixture is not saturated, some water in the wick evaporates and diffuses into the air → cooling the water in the wick
- as the temperature of the water drops, heat is transferred to the water from both the air and the thermometer
- the steady state temperature is the wet-bulb temperature

Sling Psychrometer - a rotating set of thermometers one of which measures wet bulb temperature and the other dry bulb temperature. T_{DB} and T_{WB} are sufficient to fix the state of the mixture.

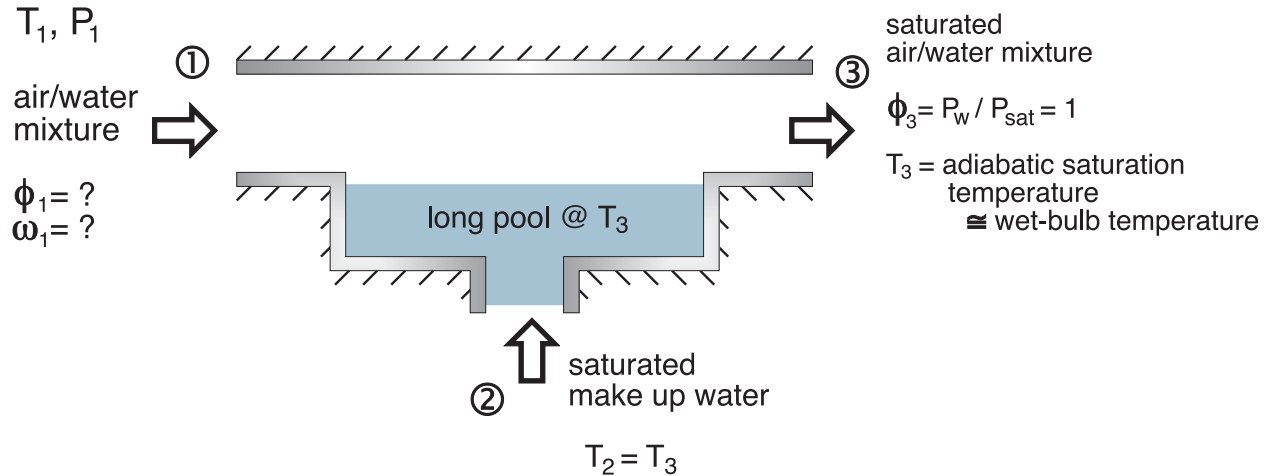
The Psychrometric Chart



where the **dry bulb** temperature is the temperature measured by a thermometer placed in the mixture and the **wet bulb** temperature is the adiabatic saturation temperature.

An Adiabatic Saturator

How can we measure humidity?



- the adiabatic saturator is used to measure humidity
- two inlets, single exit device through which moist air passes
- air-water mixture of unknown humidity enters at a known pressure and temperature
- if air/water mixture is not saturated, ($\phi < 100\%$), some water from the pool will evaporate
- the energy required to evaporate the water comes from the moist air → mixture temperature decreases
- for a sufficiently long duct, the moisture exits with $\phi_3 = 1$
- the temperature of the exiting mixture is called the adiabatic saturation temperature

Adiabatic Saturator Analysis

Conservation of Mass

$$\dot{m}_{a,1} = \dot{m}_{a,3} \quad \text{air} \quad (1)$$

$$\dot{m}_{w,1} + \dot{m}_{w,2} = \dot{m}_{w,3} \quad \text{water} \quad (2)$$

Conservation of Energy

$$(\dot{m}h)_{a,1} + (\dot{m}h)_{w,1} + (\dot{m}h)_{w,2} = (\dot{m}h)_{a,3} + (\dot{m}h)_{w,3} \quad (3)$$

By definition

$$\omega_1 = \left(\frac{\dot{m}_w}{\dot{m}_a} \right)_1 \quad (4)$$

$$\omega_3 = \left(\frac{\dot{m}_w}{\dot{m}_a} \right)_3 \quad (5)$$

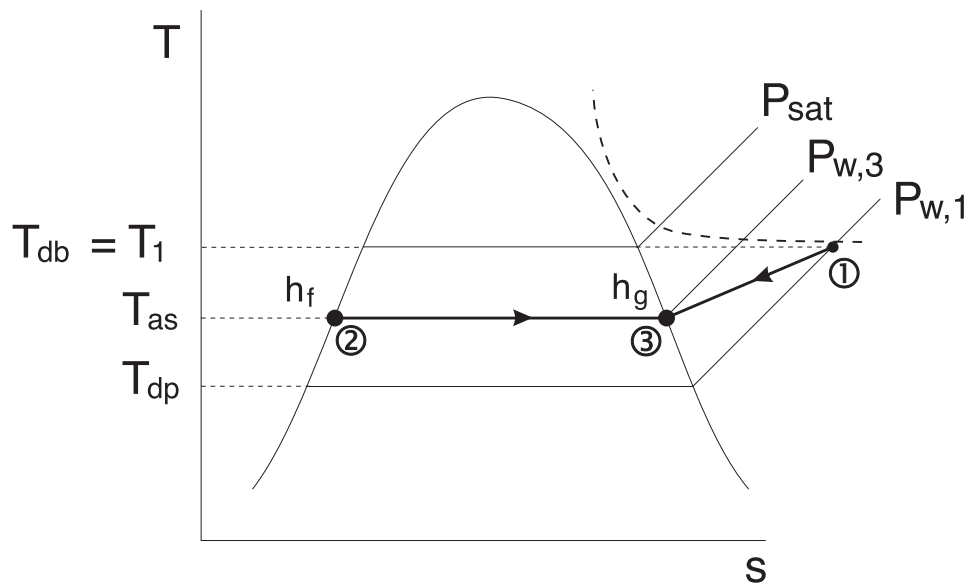
From (2) and (1)

$$\left(\frac{\dot{m}_w}{\dot{m}_a} \right)_2 = \left(\frac{\dot{m}_w}{\dot{m}_a} \right)_3 - \left(\frac{\dot{m}_w}{\dot{m}_a} \right)_1 = \omega_3 - \omega_1$$

Dividing (3) by \dot{m}_a and noting $m_{a1} = m_{a3}$ and $\frac{m_{w2}}{m_{a1}} = \omega_3 - \omega_1$

$$h_{a,1} + \omega_1 h_{w,1} + (\omega_3 - \omega_1) h_{w,2} = h_{a,3} + \omega_3 h_{w,3} \quad (6)$$

$$\omega_1 = \frac{(h_{a,3} - h_{a,1}) + \omega_3 (h_{w,3} - h_{w,2})}{(h_{w,1} - h_{w,2})}$$



If we assume:

- i) air is an ideal gas and $(h_{a,3} - h_{a,1}) = c_{p_a}(T_3 - T_1)$
- ii) $(h_{w,3} - h_{w,2}) = h_g - h_f = h_{fg}(T_3)$
- iii) $h_{w,1} \approx h_g(T_1)$
- iv) $h_{w,2} = h_f(T_2) = h_f(T_3)$

then we can write ω_1 as a function of T_1 and T_3 only

$$\omega_1 = \frac{c_{p_a}(T_3 - T_1) + \omega_3 h_{fg}(T_3)}{h_g(T_1) - h_f(T_3)}$$

Aside: Since $h_f \ll h_g$ very little is lost if the denominator is approximated as $h_{fg}(T_1)$

During the adiabatic saturation process, the vapour pressure increases and the temperature decreases; so the adiabatic saturation temperature is higher than the dew point temperature and lower than the dry bulb temperature. For the limiting case of a saturated mixture, the dry bulb, dew point and adiabatic saturation temperature are the same.

Equation 6 can be written as


$$h_1^* + \underbrace{(\omega_3 - \omega_1) h_{l,2}}_{\text{negligible}} = h_3^*$$

where

$$h^* = h_a + \omega h_w$$

Therefore $h_1^* \approx h_3^*(T_{wb})$. The lines of wet bulb temperature and h^* coincide on the psychrometric chart. Since h_3^* is solely a function of T_{wb} , lines of h_1^* are proportional to T_{wb} .

Reacting Gas Mixtures

	Reading	Problems
	15-1 → 15-7	15-21, 15-32, 15-51, 15-61, 15-74 15-83, 15-91, 15-93, 15-98

Introduction

- thermodynamic analysis of reactive mixtures is primarily an extension of the principles we have learned thus far
- it is necessary to modify the methods used to calculate specific enthalpy, internal energy and entropy

Definitions

Combustion Process:

- a fuel made up of hydrocarbons is said to have burned completely if:
 - all the carbon present in the fuel is burned to carbon dioxide
 - all the hydrogen is burned to water
- if the conditions are not fulfilled the combustion process is incomplete

Combustion Reactions:

reactants → products

or

fuel + oxidizer → products

- in all cases the mass is conserved
mass of products = mass of reactants

Fuels:

- fuel is simply a combustible substance
- hydrocarbon fuels exist as liquids, gases and solids
 - liquids → gasoline - octane, C_8H_{18}

- gases \rightarrow methane, CH_4
- solids \rightarrow coal

Combustion Air:

- oxygen is required in every combustion reaction
- in most combustion reactions air provides the needed oxygen
- dry air is considered to be

21% oxygen } on a molar basis
79% nitrogen }

$$\text{molar ratio} = \frac{n_{N_2}}{n_{O_2}} = \frac{0.79}{0.21} = 3.76$$

1 *mole* of air can then be written as $[0.21 O_2 + 0.79 N_2]$

For convenience, we typically refer to air as $[O_2 + 3.76 N_2]$ which is actually 4.76 moles of air.

Note: From the Amagat model, we know that a mixture at a known T and P (as is the case with combustion reactions)

$$\frac{n_i}{n} = \frac{V_i}{V}$$

Therefore, by expressing a mixture in terms of the number of moles we are also expressing it in terms of a volume fraction.

- nitrogen does not undergo a chemical reaction in combustion since it is inert

Air-Fuel Ratio:

$$\frac{\text{mass of air}}{\text{mass of fuel}} = \frac{\text{moles of air} \times \tilde{M}_{air}}{\text{moles of fuel} \times \tilde{M}_{fuel}}$$

$$AF = \bar{AF} \left(\frac{\tilde{M}_{air}}{\tilde{M}_{fuel}} \right)$$

where:

AF - air fuel ratio on a mass basis

\bar{AF} - air fuel ratio on a molar basis

\tilde{M}_{air} = 28.97 kg/kmole

Theoretical or Stoichiometric Air:

- the minimum amount of air that supplies sufficient oxygen for complete combustion of all carbon and hydrogen in the fuel - referred to as stoichiometric, 100% stoichiometric or theoretical
- no free oxygen would appear in the products
- greater than stoichiometric leads to free oxygen in the products
- less than stoichiometric and C , CO , OH , H_2 will appear in the products since there is not enough oxygen to form water or carbon dioxide (the actual proportions will depend on the temperature and the pressure)
- normally the amount of air supplied is given as a percentage of the theoretical value
i.e. 150% = 1.5 × the theoretical air
- referred to as 20% excess air, 120% stoichiometric

Equivalence Ratio:

- defined as

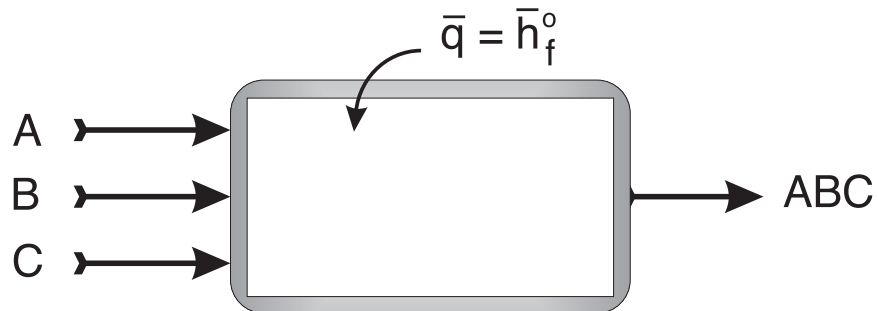
$$\text{equivalence ratio} = \frac{AF_{\text{actual}}}{AF_{\text{theoretical}}}$$

- if the equivalence ratio is:
 - > 1 → lean mixture (excess air)
 - < 1 → rich mixture (not enough air)

Conservation of Energy for Reacting Systems

Enthalpy of Formation

- previous calculations involving enthalpy were all based on differences and the reference used to determine enthalpy did not matter
- when chemical reactions occur, reactants disappear and products are formed
→ differences cannot be calculated for all substances involved
- it is necessary to establish a common base to account for differences in composition
- the enthalpy datum for reacting systems is set to zero at standard temperature and pressure
 - $T_{ref} = 25^\circ C \rightarrow 298 K$
 - $P_{ref} = 1 atm$
- $h = 0$ assigned to elements in their most stable form i.e. $O_2, N_2, C, etc.$
- **Enthalpy of Formation:** *the energy released or absorbed when a compound is formed from its stable elements at STP*



where \bar{h}_f^o is the enthalpy of formation.

Taking an energy balance over the combustion chamber shown above, we obtain

$$\underbrace{a \bar{h}_A^o + b \bar{h}_B^o + c \bar{h}_C^o}_{\text{generally}=0} + \bar{h}_f^o \longrightarrow \bar{h}_{ABC}^o$$

The left side of the equation is typically zero because $h = 0$ for elements in their stable form. The sign of \bar{h}_f^o indicates the direction of heat flow; +ve is endothermic and -ve is exothermic.

Effects of Non-Standard Temperature

$$\bar{h}(T, P) = \bar{h}_f^\circ + \underbrace{(\bar{h}_{T,P} - \bar{h}_{T=25^\circ\text{C}, P=1\text{ atm}}^\circ)}_{\Delta\bar{h} \text{ at known temperatures}}$$

where

\bar{h}_f° is the heat resulting from a chemical change at $T = 25^\circ\text{C}$ and $P = 1\text{ atm}$

$\Delta\bar{h}$ is the heat resulting from a change in temperature (sensible heat) with respect to the reference temperature, $T_{ref} = 25^\circ\text{C}$

Enthalpy of Combustion

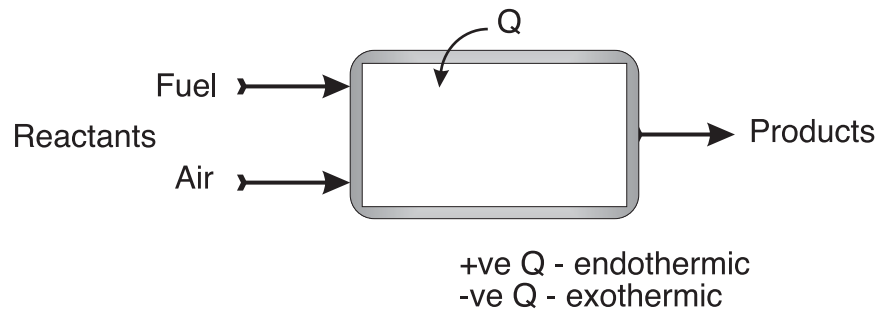
- while the enthalpy of formation is related to elemental reactants \longrightarrow resulting in a single compound; the **enthalpy of combustion** is related to *fuel + oxidizer* as the reactants
- **Enthalpy of Combustion:** *the difference between the enthalpy of the products and the enthalpy of the reactants where complete combustion occurs at a given temperature and pressure*

$$Q = \sum (mh)_P - \sum (mh)_R = \underbrace{H_P(T_P) - H_R(T_R)}_{H_{RP}}$$

$$Q = \sum (n\bar{h})_P - \sum (n\bar{h})_R = \underbrace{\bar{H}_P(T_P) - \bar{H}_R(T_R)}_{\bar{H}_{RP}}$$

where

$$\bar{h}_c = H_{RP} / \text{kmole of fuel}$$



with:

+ve Q \Rightarrow *endothermic*

-ve Q \Rightarrow *exothermic*

- when enthalpy of formation data are available for all products and reactants the above equation can be used
- otherwise a calorimeter must be used to measure the enthalpy of combustion

Heating Value

- the heating value of a fuel is a positive value equal to the magnitude of the enthalpy of combustion when products are returned to the state of the reactants
- two values are used
 - **HHV**: higher heating value - obtained when all the water formed by combustion is a liquid at the reference temperature
 - **LHV**: lower heating value - obtained when all the water formed by combustion is a vapour as an ideal gas in the mixture of the products
- the HHV exceeds the LHV by the energy required to vaporize the liquid formed

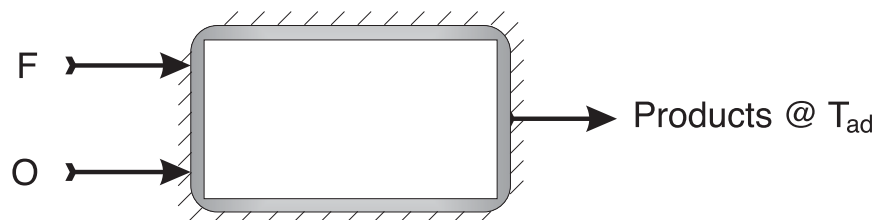
$$\begin{aligned} HHV &= LHV + \frac{(m \cdot h_{fg})_{H_2O}}{\text{kmole of fuel}} \\ &= LHV + (\tilde{M} \cdot h_{fg})_{H_2O} \cdot \frac{n_{H_2O}}{n_{fuel}} \end{aligned}$$

where

$$h_{fg}(25^\circ C) = 2,442.3 \text{ kJ/kg}$$

$$\tilde{M}_{H_2O} = 18.015 \text{ kg/kmole}$$

Adiabatic Flame Temperature



- if the system is perfectly insulated it cannot dispose of the LHV and the LHV goes into heating the products above the reference temperature

- under adiabatic conditions, the maximum temperature attained by the products when combustion is complete is called the adiabatic flame or adiabatic combustion temperature

$$H_P(T_{ad}) = H_R(T_R)$$

$$\sum_P n_P (\bar{h}_f^o + \underbrace{\bar{h} - \bar{h}^0}_{\Delta \bar{h}})_P = \sum_R n_R (\bar{h}_f^o + \underbrace{\bar{h} - \bar{h}^0}_{\Delta \bar{h}})_R$$

We need to collect terms based on what we know or can readily calculate and what we do not know, i.e. terms that are a function of T_{ad} .

$$\begin{aligned} \sum_P \underbrace{n_P (\bar{h})_P}_{\substack{\text{sensible heat} \\ \text{function of } T_{ad}}} &= \sum_R \underbrace{n_R (\bar{h} - \bar{h}^o)_R - \left(-\sum_P n_P (\bar{h}^o)_P \right)}_{\substack{\text{sensible heat} \\ \text{function of } T_R \text{ or } T_{ref}}} \\ &+ \sum_R \underbrace{n_R (\bar{h}_f^o)_R - \sum_P n_P (\bar{h}_f^o)_P}_{\substack{\text{chemical heat} \\ \text{function of } T_R \text{ or } T_{ref}}} \end{aligned}$$

Step 1: Calculate the right hand side based on known values of T_R and T_{ref} .

Step 2: Calculate the left hand side based on a guessed value of T_{ad} .

Step 3: Repeat Step 2, until LHS = RHS.

Dew Point

- since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapour in the form of gaseous products can be significant
- if the gaseous products of combustion are cooled at constant mixture pressure the dew point temperature is reached when water vapour begins to condense
- since corrosion of duct work, mufflers etc. can occur, the knowledge of dew point temperature is important

Evaluation of Entropy for Reacting Systems

The 2nd law entropy equation can be written as

$$\underbrace{S_{in} - S_{out}}_{\text{due to heat \& mass transfer}} + \underbrace{S_{gen}}_{\text{generation}} = \underbrace{\Delta S_{system}}_{\text{change in entropy}}$$

For a closed system, such as a combustion process, the entropy balance on the system can be written as

$$\sum \frac{Q_i}{T_i} + S_{gen} = S_P - S_R$$

- a common datum must be used to assign entropy values for each substance involved in the reaction
- an entropy of 0 for pure crystalline substances is obtained at absolute zero
- the entropy relative to this datum is called absolute entropy
- absolute entropy at 1 atm and temperature T is denoted as $s^o(T)$ or $\bar{s}^o(T)$ for a per unit mass or per mole basis
- while \bar{h} was only a function of temperature for ideal gases, we must account for the effects of both T and P in entropy

- the entropy at any value of T and P can be calculated as

$$\bar{s}(T, P) = \underbrace{\bar{s}^o(T)}_{\text{tables}} - \mathcal{R} \ln \left(\frac{P_i}{P_{ref}} \right)$$

where

$$P_{ref} = 1 \text{ atm}$$

$$P_i = \text{partial pressure of } i\text{'th component}$$

$$\mathcal{R} = 8.31434 \text{ kJ/kmole} \cdot \text{K}$$

- the partial pressure P_i can also be written as

$$P_i = Y_i P$$

and

$$\bar{s}(T, P_i) = \bar{s}_i^o(T) - \mathcal{R} \ln \left(\frac{Y_i P}{P_{ref}} \right)$$

where P is the mixture pressure and Y_i is the mole fraction of the $i\text{'th}$ component.